Thur Exam - Jan. 30
1:30 P.M.

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84 define a slag
87 Silicate degree
103-112 97 ~~Cupellation~~ spitting - just starts
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Scorification
Various methods

4 methods for calc.

2 things aim for in slag

Pb, Speiss, Mono silicate
Cu Ni — Sub silicate
over 25% Sulphur use $\frac{1}{4}$ under use $\frac{1}{2}$

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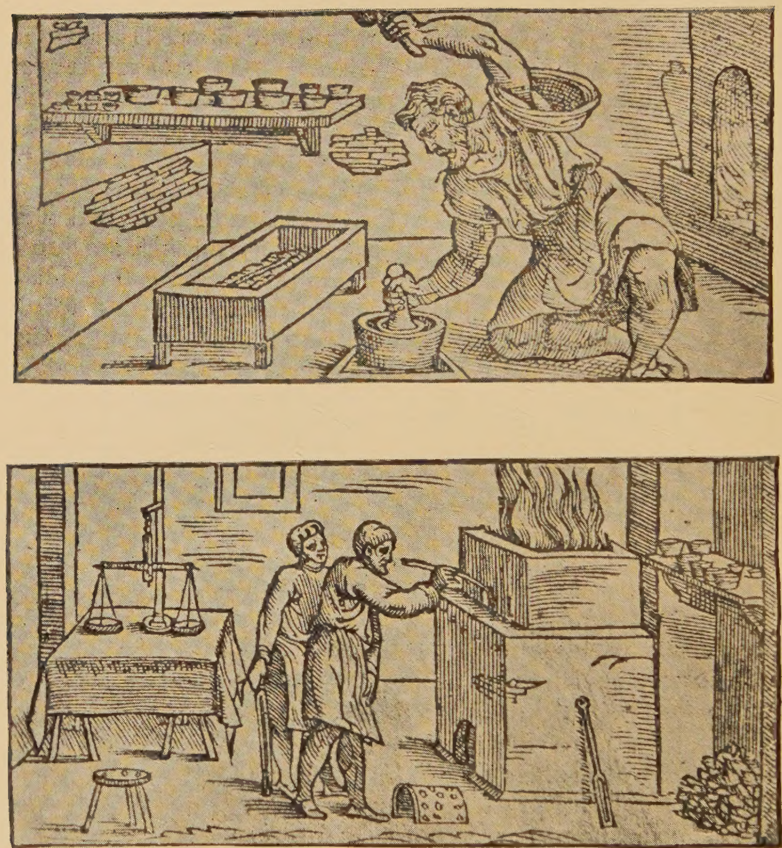
METALLURGICAL TEXTS

A MANUAL OF FIRE ASSAYING

METALLURGICAL TEXTS

A SERIES OF TEXTBOOKS OUTLINED BY THE

FOLLOWING COMMITTEE



The Assayer.—From Pirotechnia, Li Diece Libri Della Pirotechnia, by Vannuccio Biringoccio, Venice, MDLVIII.—(3rd edition).

A MANUAL
OF
FIRE ASSAYING

BY

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Entirely Rewritten and Enlarged
Fifth Impression

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[DEDICATION OF THE FIRST AND SECOND EDITIONS]

To His Mother

THIS BOOK IS LOVINGLY DEDICATED BY

THE AUTHOR

PREFACE TO THE THIRD EDITION

This edition of "A Manual of Fire Assaying" is thoroughly revised, in part rewritten, and considerable new matter has been added. This is particularly true of the chapters on "Assay Furnaces and Tools," "Reagents," "Parting and Inquartation," and "The Assay of Platinum and Related Metals." Dr. W. J. Sharwood, Chief Chemist of the Homestake Mining Company, has joined the author of the first two editions as a coauthor in the Third Edition. The authors wish to express to Miss Dorothy Kiesler their appreciation for the assistance rendered in the preparation of the manuscript.

THE AUTHORS.

ROLLA, MO.,
April, 1929.

PREFACE TO THE FIRST EDITION

The author has long recognized the need of a work on fire assaying that treats the subject from the scientific and rational point of view rather than from that of the "rule of thumb." Strangely enough, this last governs most modern works on the subject. The book is closely confined to the subject of fire assaying, which it treats in detail. The chapters on Reduction and Oxidation Reactions, Crucible Assay and Assay Slags, and Cupellation outline scientifically the principles of assaying. A large part of these chapters is new and some of the material is presented for the first time. The chapter on the Errors in the Assay for Gold and Silver discusses the accuracy of the assay in greater detail than has been attempted heretofore.

The author has had experience with practically all of the methods of assay described in the book; first as a manipulator, then as a teacher, and finally in charge of works. The book is intended for the use of students in technical schools and for the assayer in actual daily practice who may feel the need of a reference book.

The author wishes to acknowledge his indebtedness to the writers cited in the text, especially the late Prof. E. H. Miller, of Columbia University, whose work and personality have ever been an inspiration to the author. He also expresses his thanks to Mr. J. B. Read and Mr. Ivan E. Goodner, chemist and assayer, respectively, for the Standard Smelting Company, Rapid City, and to Mr. Frank Bryant, his assistant at the School of Mines, for valuable aid in the testing of methods; to Prof. M. F. Coolbaugh for the inspection of those chapters containing chemical equations, etc.; and to Miss Ethel Spayde and Miss Della M. Haft for valuable aid received in the preparation of the manuscript for publication. The author also desires to express his

appreciation of the courtesy of the Denver Fire Clay Company and of Ainsworth & Son, Denver, Colo., of F. W. Braun and Company, Los Angeles, Calif., and of others, in furnishing photographs and electrotypes of apparatus used in the book.

CHARLES H. FULTON.

RAPID CITY, S. DAK.,
April, 1907.

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A MANUAL OF FIRE ASSAYING

CHAPTER I

INTRODUCTORY CHAPTER; DEFINITIONS. OUTLINE OF PROCESSES OF ASSAYING

Assaying includes all those operations of analytical chemistry which have for their object the determination of the constituents of ores and metallurgic products. Three methods are used: (1) fire assaying (dry methods); (2) gravimetric analysis (wet methods); (3) volumetric and colorimetric analysis (wet methods). This work treats of fire assaying only, with a few exceptions. The quantitative determination of the following metals is discussed: gold, silver, platinum, etc., lead, antimony, bismuth, tin, copper, and mercury; chiefly, however, gold and silver.

Fire assaying comprises the separation of the metal sought from the other components of the ore, by heat and suitable fluxes, and then the weighing of it in a state of greater or lesser purity.

Gold and Silver.—Gold and silver are determined in their ores, or metallurgic products, by collecting them with lead, forming an alloy, which may be accomplished either by the crucible or by the scorification fusion, the lead then being driven off by cupellation, and the resultant bead of the gold and silver alloy weighed. The separation of gold from silver is accomplished by parting, in most instances, with nitric acid, rarely by sulphuric acid.

In order successfully to collect the precious metals by means of lead, it is essential that the ore be mixed with suitable fluxes, so that in fusion the ore is thoroughly decomposed chemically, and a liquid slag of the proper constitution produced, enabling the lead with its alloyed gold and silver to settle from the slag by gravity, thus affording a ready separation.

For the purpose of orienting the student or reader, a brief outline descriptive of assay processes is given in the following pages.

Crucible Assay for Gold and Silver Ore. Outline of the Process.—A weighed amount of pulverized ore (commonly 15 to 60 g.) is mixed with a flux, consisting usually of sodium carbonate, lead oxide, and borax, together with enough carbon (or other reducing agent if the ore contains none) to reduce most of the lead oxide to metal. The mixture is fused in a fire-clay crucible at a red heat until the lead separates and sinks through the mass, carrying with it the precious metals, while the silica, alumina, etc., in the ore form a slag with the remaining constituents of the flux. The whole is poured into a mold and allowed to cool and solidify. The lead button is then separated and placed in a cupel of bone ash (or other porous refractory material) previously raised to a red heat in a muffle. Here it is heated under oxidizing conditions, so that the lead is oxidized and absorbed, leaving the gold and silver, which are weighed together.

The button of gold plus silver is then flattened and treated with nitric acid to remove the silver, leaving spongy gold, which is washed, dried, heated, and weighed, the loss indicating silver. In case relatively little silver is present, more must be alloyed with the button, as gold protects silver from the action of acids. If silver is not to be determined, the extra silver may be added before cupellation or placed in the crucible. This is an advantage, as this silver helps to collect gold during cupellation. In the case of silver ores containing no gold the acid parting is of course omitted.

The character of flux and cupel, the temperature, and other conditions of melting and cupelling influence the results and must all be closely controlled. The whole art of assaying consists in maintaining the most favorable conditions at each stage of the process and obtaining the maximum gold and silver in a pure state for weighing.

Scorification Assay.—A small portion of ore (usually 1 to 6 g.) is mixed with granulated pure lead in a shallow clay vessel (scorifier) and strongly heated in a muffle with free access of air. The lead partly oxidizes and the oxide fuses, combining with the oxidized base metals and silicates of the ore to form a slag, while the precious metals and part of the copper, etc., alloy with the remaining lead. This is poured into a mold and cupelled, etc., as in the crucible assay.

Assay of Gold and Silver Bullion: the Cupellation Process.—The bullion may contain gold or silver or both, together with base

metal in any proportion. A small quantity, usually 500 mg., is weighed out and wrapped in 5 or 10 g. of pure sheet lead and placed in a small porous cup or cupel of bone ash, previously heated to redness in a muffle or open furnace; the lead and other metals are oxidized and the fused oxides are absorbed by the cupel, leaving the gold and silver which are weighed together, the loss being considered base metal. If the proportion of silver is more than double that of the gold, the operation of "parting" may be carried out at once. The "button" is flattened and rolled out thin, heated to soften it, coiled into a close roll or "cornet," and then subjected to the action of hot nitric acid, somewhat diluted. This removes the silver, leaving soft, spongy gold, which is washed with water, dried and heated to a dull-red heat. The last operation is called *annealing*, and leaves the gold yellow and coherent, so that it can be handled and weighed; silver is estimated from the difference of the two weighings. In case the proportion of silver to gold is small, the gold would protect it from the attack of the acid, and it is necessary to add more silver before parting. This operation is known as *inquartation*, as it was formerly thought that the best proportion of gold for parting was one-quarter of the total weight. It is usually effected by wrapping the cupelled button and additional silver in a little lead foil and again cupelling. The inquarted button is then ready for parting, etc.

The resulting "fineness" is reported as so many parts of gold and of silver per thousand of original bullion. If carried out in duplicate on 500-mg. samples, the sum of the duplicate weighings in milligrams gives the fineness directly.

To save time, it is customary to weigh out four lots of bullion; two of these are cupelled with lead alone, two are, at the same time, inquarted with sufficient silver for parting. The first two are weighed as "doré," or gold plus silver, while the two latter are parted, and the gold annealed and weighed alone. Also, as slight errors are introduced in the above separation, these are corrected in exact work by means of "proofs." The proofs are made by weighing out pure gold, silver, and copper to imitate the assay pieces as nearly as possible, and they are treated side by side with the assays in precisely the same manner. Any loss or gain suffered by the proof is assumed to apply also to the assay proper, which is corrected accordingly.

Solutions.—In the assay of solutions, several methods are available. One of the best is to take a measured volume (say, 100 to 500 cc.), add a lead salt (*e.g.*, 20 or 30 g. of lead acetate), heat and add about 10 g. of zinc dust, finally adding 20 or more cc. of strong hydrochloric acid. Spongy metallic lead is thus precipitated, carrying with it all the gold and silver present. On separating the lead completely, as by filtration or even by removing it with the fingers and squeezing it, these metals are isolated; the lead alloy may then be scorified a few minutes and finally cupelled, etc., as already described.

With solutions, a rather large quantity of sample can be conveniently handled (say, 300 to 1,000 cc. or more), and the limit of accuracy is thus increased.

Lead Ores.—A convenient amount, say 10 g. of pulverized ore, is mixed in a crucible with a flux, usually sodium and potassium carbonate, with a little borax and some reducing agent, such as flour or argol (potassium acid tartrate). Iron may be added as a desulphurizer. Upon fusion, the lead is reduced to a fusible button, which, after cooling, can be detached and weighed. Incidentally, any gold or silver present is concentrated in this button.

Tin Ores.—Fusion with an excess of alkaline cyanide reduces tin oxide to metal, the cyanide being at the same time partly oxidized to cyanate, while sulphides yield thiocyanate:

$$\mathrm{O + NaCN = NaCNO}$$
$$\mathrm{S + NaCN = NaCNS}$$

The button of metallic tin is separated, washed, and weighed. The same method is available for ores of antimony, bismuth, and lead. Ores containing coarse metallic copper are sometimes fluxed with borax and sodium carbonate, and the melted metal is collected and weighed directly.

Mercury Ores.—Mercury differs from most metals in being easily distilled as well as easily reduced; this property is utilized in the assay of its ores. The ore, from 0.1 to 100 g., is mixed with quicklime or metallic iron. On heating to low redness, the metal is reduced and vaporized; it may be condensed in a glass condenser and collected for weighing, or it may be absorbed by a weighed sheet of metallic gold or silver.

CHAPTER II

ASSAY FURNACES AND TOOLS

FURNACES

The furnaces used in assaying are many in design, varying mainly with the kind of fuel used. They are classified as follows: (1) pot furnaces, in which the assay is in direct contact with the fuel or products of combustion, (2) muffle-furnaces, in which a muffle or receptacle containing the assay is externally heated.

As the muffle furnace is practically essential[1] for carrying on the operations of scorification and cupellation, and crucible fusions can be made satisfactorily in the muffle if it be large enough, muffle furnaces have largely replaced pot furnaces for general assaying. In general, they are cleaner, more easily operated, better controlled as to temperature, and, if large enough, are of great capacity, which makes them especially desirable for smelter, mill, and mine assay offices, where frequently a great number of assays are performed daily. The choice of fuel for heating the furnaces is usually dependent on locality. Bituminous and lignite coal, coke, anthracite, crude oil, gasoline or kerosene, wood, fuel and illuminating gas are all used as well as electric heating. Of these, coke and anthracite are the fuels least desirable for muffle furnaces, for burning without flame they must surround the muffle. This makes the firing difficult, requiring considerable attention. The best fuel, usually, also, the most easily obtainable, is bituminous or good lignite coal, yielding a long or reasonably long flame. One-, two-, and three-muffle furnaces, constructed of fire-clay tiling, fire brick, and common hard brick, tightly bound with stays and rods, are in common use and for general utility, where much work must be performed, are very desirable.

Coal, Coke, and Oil Furnaces.—Figures 1 and 2 show such a two-muffle furnace in cross-section. The essential parts of the

[1] "Koenig's Furnace," *Trans.* A. I. M. E., vol. XXVIII, p. 271. This furnace is practically a pot furnace fired by gasoline and with an air blast can be used to scorify and cupel without a muffle.

furnace, as the tiling, *A*, *B*, *L*, *K*, etc., can be readily purchased, although the interior of the furnace may also be built of fire brick. The tiling furnace, however, is more easily set up and is more durable. In the design of the soft-coal furnace, the essential dimensions are: area of fire grate; distance from the grate to the bottom of the lower muffle; "fire space," *i.e.*, the distance

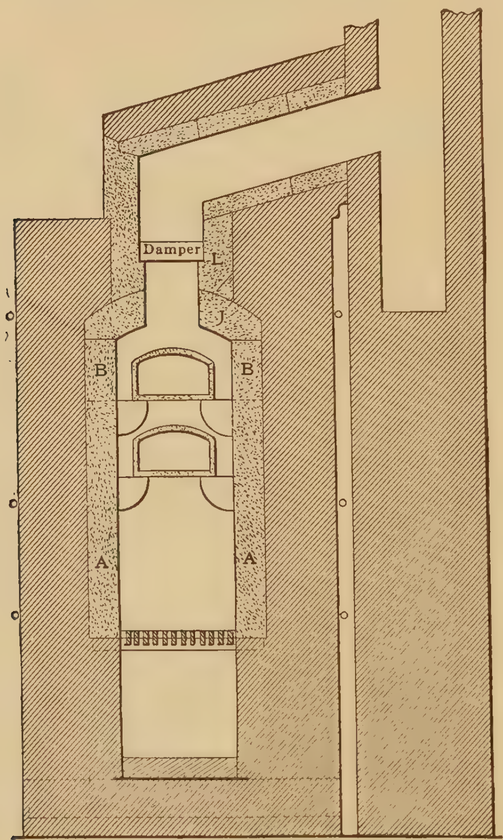

FIG. 1.—Two-muffle furnace. Cross-section.

between muffles and the side and end walls of the furnace and between the top of the upper muffle and the roof of the furnace, giving the proper space for combustion of the gases. These dimensions depend upon the nature of the coal. In Figs. 1 and 2, the grate dimensions are 17.25 by 21.0 in.; distance from grate to lower muffle, 18 in.; fire space, 2.5 in.; external dimension of muffle, 19 in. long, 12.25 in. wide, 7.75 in. high. The flue area

should be from one-sixth to one-eighth of the grate area. The flue is best placed forward of a line through the center of the muffles to get the full sweep of the flame around them, although if the draft is poor this arrangement is apt to cause smoky muffles.

The walls of the furnace are thick (13 in.) to prevent radiation. The front of the furnace above the muffle is arched. The arch tiling has in it a duct, leading to the flue, to carry off any lead fumes which may escape at the mouth of the muffle. The muffles are supported by two sets of cantilever tiles or jamb

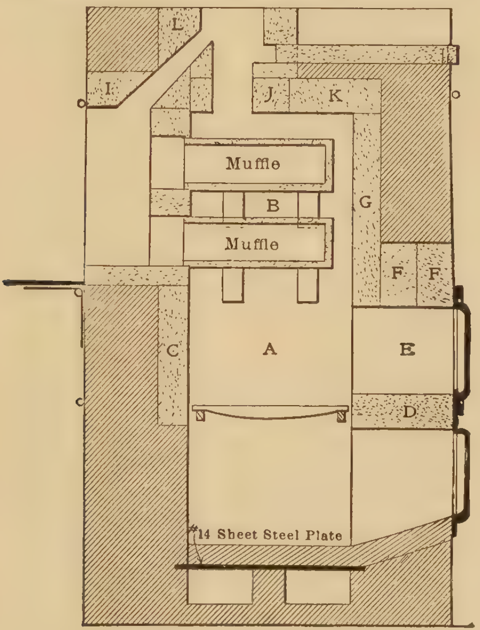

FIG. 2.—Two-muffle furnace. Longitudinal section.

brick, placed into the side walls, and sometimes by an additional set in the rear end wall. These tiles frequently prove weak and, in falling away, leave the muffle without support, causing it to be short lived. The supports are best made in such shape, of two pieces, that they will join under the center line of the muffle and arch over, supporting each other. The writers have used supports of this type, which were perfectly satisfactory and increased the life of the muffles greatly. A furnace of the kind described has a capacity of 25 to 30 fusions (20-g. crucible) per hour, including the necessary cupellations. If the fusions are

made in 30-g. crucibles or in 2.5-in. scorifiers, the capacity is from 20 to 24. With good draft, this furnace burns from 37 to 47 lb. of coal per hour, which, at $7 per ton, makes the cost per assay for fuel amount to from 0.80 to 1.00 ct., when assaying continuously and somewhat more when the furnace is not charged to its maximum capacity. With a good grade of coal (6,500 to 7,500 cal. or 11,700 to 13,500 B.t.u.), a maximum temperature of 1150° to 1200° C. can be obtained in this furnace after 4 hours' firing.

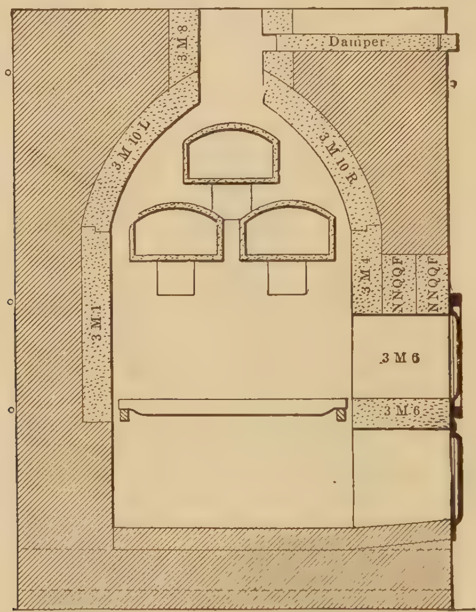

FIG. 3.—Three-muffle furnace. Cross-section.

Figures 3 and 4 show a three-muffle furnace of similar type fired from the side.

Coal furnaces may also be readily modified to burn crude oil. This can be done by placing tiling in the fire box and making the necessary pipe and burner connections.[1]

Figure 5 shows such a furnace. The burner is a ¾-in. pipe connected by a T to the oil line, also a ¾-in. pipe. A ¼-in. steam pipe passes into the burner pipe at the rear through a packing nut which permits of the adjustment of the distance

[1] BOWMAN, F. C., "Crude Oil for Fire Assaying," *Proc.* Colo. Sci. Soc., vol. VII, p. 341.

between the nozzle of the burner pipe and the nozzle of the steam pipe. By varying this distance, the flow of oil may be controlled independently of the steam and oil inlet valves. The nozzle of the burner pipe is a ¼-in. hole, and that of the steam pipe a ⅛-in. hole.

The grate bars in the furnace are covered with fire brick, as shown in the illustration. The placing of the fire brick is of importance, as the successful working of the furnace is dependent upon their position.

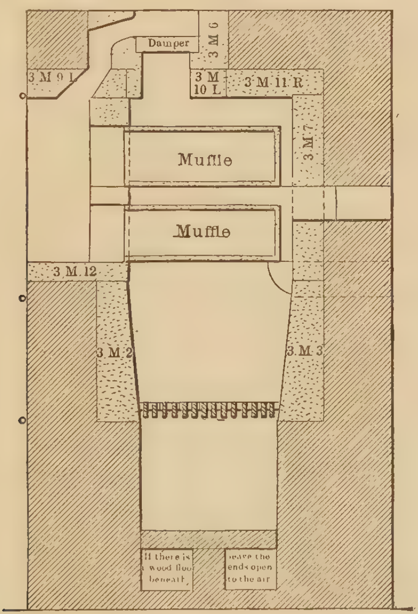

FIG. 4.—Three-muffle-furnace. Longitudinal section.

In starting the fire, a piece of oiled waste is lighted in the fire box just behind the burner. When the waste is burning well, oil and steam are turned on simultaneously. The oil and steam valves are then set to give the proper flow. Plenty of waste should be used to furnish a blaze until the fire box is hot enough to ignite the oil; otherwise, explosions are apt to occur. The steam used should be dry, and to insure this the steam pipe leading to the burner may be passed around the flue, as shown in the figure. The valve DV at the end of the steam line is kept slightly open during working to permit the escape of water of condensation. A small steam coil may also be placed in the

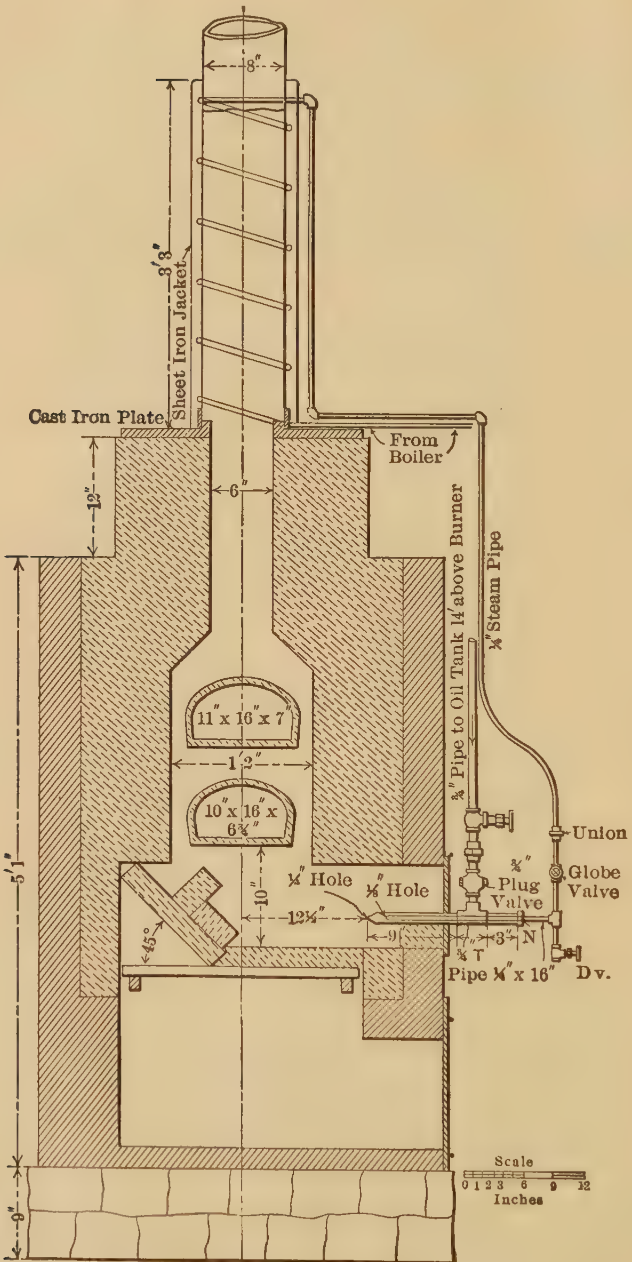

FIG. 5.—Converted oil-burning furnace. The burner may also be placed at the front or rear of the furnace; as a rule the rear is the more convenient location.

oil tank to keep the oil more fluid. The furnace may be heated to a red heat 15 to 20 min. after starting. The furnace has a capacity of 25 to 30 assays, including cupellations in 1¾ to 2 hours and 50 to 60 assays in 3 hours. The amount of oil used varies from 4.2 to 5.3 gal. per hour. With oil at 8½ cts. per gallon, the cost per assay for fuel is 2.2 to 2.8 cts.

Figures 6 and 7 show a wood-burning muffle furnace. In some districts, wood is the only available cheap fuel. If the fire box and fire spaces are properly designed (*i.e.*, of larger size than in the

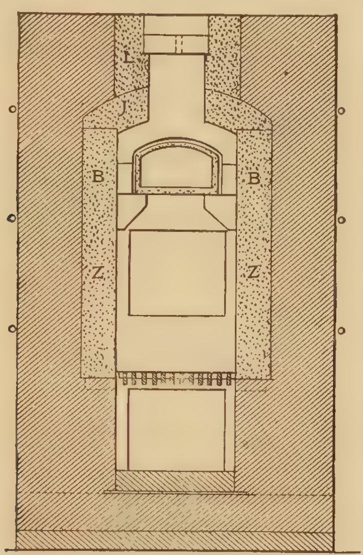

Fig. 6.—Wood-burning-muffle-furnace. Cross-section.

coal furnace) and a deep bed of fuel is provided for (*i.e.*, the distance from the grate surface to the bottom of the fire door is from 8 to 10 in.), sufficient temperature for ordinary assaying can be attained in this type of furnace. Almost any wood may be used, but it should be as dry as possible to avoid the cooling effect of vaporizing water. After most of the water and resinous material has been driven off, the residue is essentially charcoal, or nearly pure carbon, and burns in the same way.

In the furnace shown in Figs. 6 and 7, the grate is 18 in. wide and 26 in. long; the distance from the grate bars to the bottom of the muffle is 26 in., and the fire space is 2.5 in. wide at the sides and 3.5 in. at the top. Figure 8 shows a wood-burn-

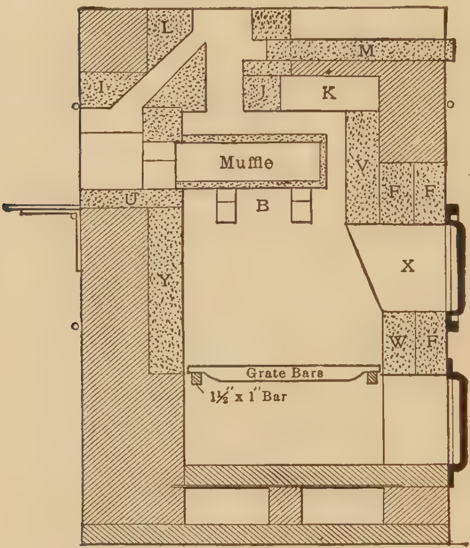

FIG. 7.—Wood-burning-muffle-furnace. Longitudinal section.

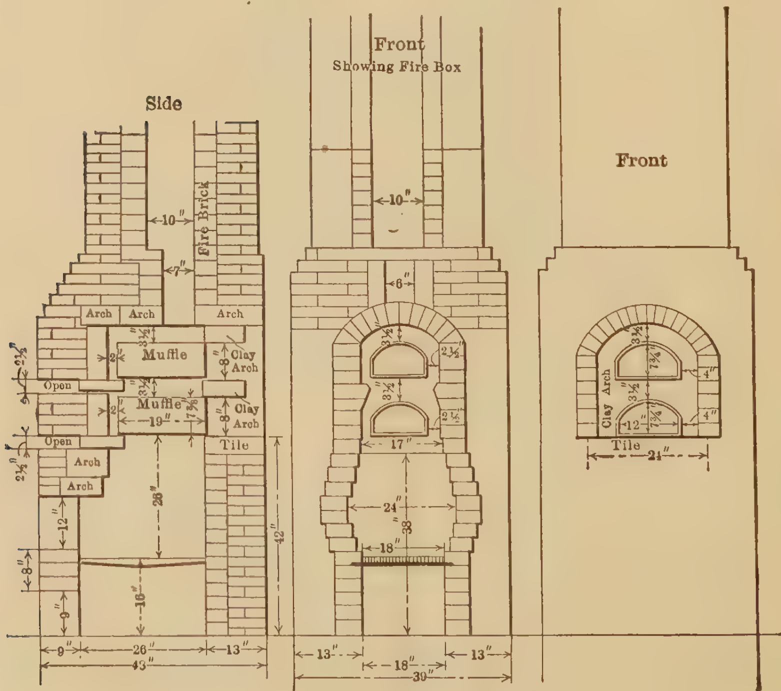

FIG. 8.—Wood-burning muffle-furnace.

ing furnace of somewhat different construction.[1] With piñon pine or fir wood at $4.50 per cord, the cost of fuel is 65 cts. for a daily run of 30 to 40 assays. With a poor grade of wood at $6.50 per cord, in another instance, 30 assays cost 93 cts., or 3.1 cts. per assay, including cupellations.

Coke and anthracite muffle furnaces when used are usually smaller, although large furnaces may be specially designed and built of the general type of the coal furnaces described.

Figure 9 shows a small coke or anthracite furnace. Most of the fuel is fed in at the top and kept well heaped around the muffle. A little is occasionally pushed in at the lower opening under the front of the muffle. A furnace of the kind shown in Fig. 9 will consume from 32 to 38 lb. of coke per hour, according to draft. With a muffle 11 by 16 by 7 in., 10 assays per hour, including cupellation, can be made at a cost of 1.7 cts. per assay with coke at $10 per ton. Charcoal may be used in this furnace in place of coke.

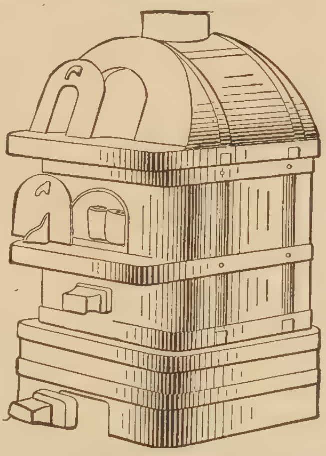

FIG. 9.—Muffle-furnace for burning coke.

Fire-clay muffles for furnaces are made in varying sizes and shapes. The best shape for general use is one of nearly rectangular cross-section, with but a slightly arched top. The largest muffles ordinarily used are 19 in. long, 14.5 in. wide, and 7.75 in. high (outside dimension). Muffles 19 in. long, 12 in. wide, and 7.75 in. high are very common in coal furnaces. The muffles have two holes in the rear end to induce an air draft through them. In some cases the outlet hole is made in the top of the muffle, toward the rear end, and surmounted by a short chimney. This may be made of a crucible with the bottom cut off.

The method of support of the muffle in the furnace has great bearing on the life of the muffle. Muffles inadequately supported soon crack and fall to pieces. It is, perhaps, better to support muffles by one substantial, rather broad support near the middle and across the whole bottom and by resting the front end on the furnace wall and the rear end on two replaceable

[1] NUTTER, E. H., *Mining Sci. Press*, vol. XCII, p. 329; JANIN, LOUIS, JR., *Eng. Mining Jour.*, vol. LXXIV, p. 810.

clay supports than to have more numerous supports extending short distances only beyond the walls on the bottom. Muffles should be stored in a dry, warm place to prevent their absorbing moisture, and when new muffles are placed in a furnace, it should be fired lightly with wood chips for an hour to anneal the muffles before heavy firing is begun. The spilling of slag and lead in the muffle rapidly leads to corrosion and softening of the bottom and consequent destruction. To avoid this deterioration in part, muffle bottoms should be covered with a layer about ¼ in. thick of bone ash, silica sand, or portland cement, to act as an absorbent. Muffles are also subject to destruction from the fluxing action of the ashes of the fuel burnt on the grate. Ashes high in iron oxide are the worst in this respect.

Muffles of carborundum are now coming into common use. While the first cost is higher, a carborundum muffle outlasts fire clay several times and a greater conductivity makes it work faster. Such a muffle, in daily use with oil fuel, will last over a year if carefully handled. The cost is approximately five times that of fire clay.

Muffles fired with gas or liquid fuel may be supported on legs or props resting on the furnace bottom and 6 to 10 in. high. These may be of fire brick, e.g., *soap* brick (about 2 × 2.25 in.), or of carborundum molded in triangular sections. They must be so placed as to distribute the flame equally.

In setting muffles, it is essential for the attainment of the best heating conditions thoroughly to lute up the space around the edge of the muffle and the arch opening in the front of the furnace into which it fits. If this space be of considerable size, it is best filled in roughly with chips of broken crucibles, etc., before applying the luting material. Luting material may be of fire clay and crushed fire brick or crucibles, one-fourth of the former to three-fourths of the latter, mixed with sufficient water to make a plastic mass. The fire brick may be crushed to pass an eight-mesh screen. Raw fire clay has a shrinkage too great to be used alone. One-quarter fire clay, one-quarter shredded asbestos, and one-half crushed fire brick make a good luting material.

Figure 10 represents a combination of crucible pot furnace and muffle furnace, such as is used in England. It may be built of ordinary fire brick and is dimensioned in such a manner as to avoid cutting brick as much as possible. It is fired by *coke*. The two crucible furnaces *S* connect with the main flue, 9 by 9 in. in size, by the flues *N*. The crucible furnace nearest the

muffle also connects with the muffle furnace by the extra flue *O*. By these means, the hot gases of combustion may be diverted to the muffle furnace, instead of directly to the stack. The pot furnaces are 14 by 14 in. in section and, on account of the sloping top, are 17 in. deep at the front and 23 in. at the back. The top of the furnace is best made of cast iron or of a sheet-steel plate cut, as required. The doors or covers are made of two tiles, each 20 by 10 by 4 in., held together by two pieces of 1.5-in. channel iron clamped by two 0.5-in. rods. To the ends of these rods, four 3-in. iron wheels are fastened on which the doors run. The tiles are secured in the frame in such a manner that there is a clearance of 0.25 in. above the furnace top so that doors may

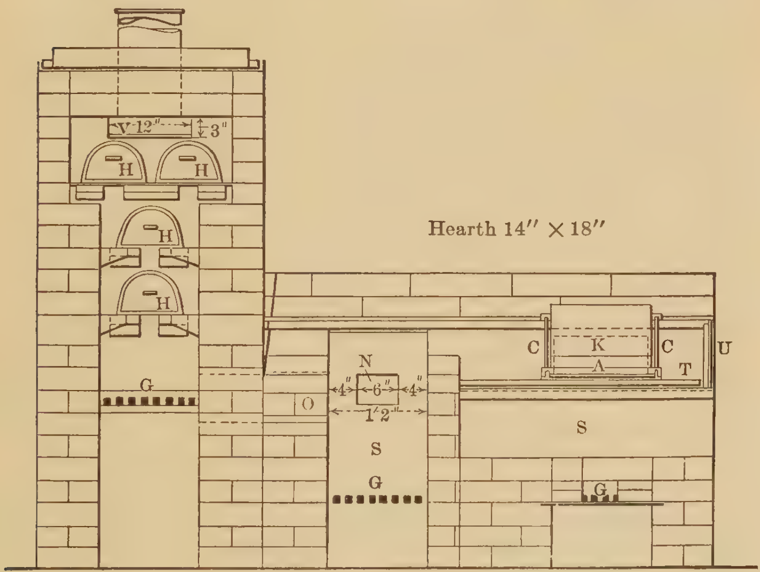

FIG. 10.—Combination muffle and pot-furnace.

move freely. Each furnace has eight grate bars of 1-in.-square wrought iron resting at the ends on two similar bars, placed on the brick-work. The bars are 14 in. long, except the two center ones which are 18 in. long, and may be withdrawn through the opening *G* for dumping the fire.

There are four muffles *H* in the furnace, 15 by 9 by 6 in. outside measurements. The lower muffle and, perhaps, the next upper one may be used for scorification and cupellation. The other two muffles will not heat to a high enough temperature for anything except annealing and roasting. The muffles rest at the

back and sides on the ends of bricks cut to a level, as shown, and projecting from the furnace body. At the front they lie flush on 1.5-in. angle irons *A*.

The furnace is built with the front entirely open; the grate bars are the same as described for the crucible furnace. When the muffles have been placed in position, the space around the front of the muffles is filled with a mixture of fire clay and silicate of soda to a depth of 3 in. A strong solution of silicate of soda or "water glass" is mixed with three times its weight of water until homogeneous. This solution is then mixed with fire clay to a stiff paste; usually, 1 part of solution is required for 7 parts of fire clay. The mixture usually contracts on heating and shrinks away at the edges. These cracks then have to be filled again.

The top of the muffle furnace is covered with tile laid in 1.5-in. angle irons A'. The flue *V* from the muffle furnace into the stack is 12 by 3 in. in size. The draft of the furnaces is controlled by placing sheet-iron plates in front of the ash-pit doors.

Reverberatory Furnaces.—These have come into use in South Africa for direct melting in crucibles and also for muffle work; similar furnaces have been used elsewhere but have never come into general use in the United States. McArthur Johnston[1] describes a reverberatory with a flat hearth for fusions, heated by long-flame coal (12,000 B.t.u., 20 to 25 per cent volatile and 12 per cent ash); the arch is 10 to 12 in. high and the working section apparently about 3 ft. square. In the corresponding muffle furnace, three small muffles are supported by flat bricks over a similar hearth, a fourth on the same level is carried by jamb brick above the grate bars, and below this a larger muffle. A muffle furnace of similar type with forced draft was formerly used at Cripple Creek. H. C. Parmelee[2] states that this, with four muffles, had a capacity of 500 to 600 assays per day of 10 hours, burning 5 tons of coal per month. Fusions were made in the muffle nearest the fire, scorifications in the second, and cupellations in the ones nearest the stack. A similar wood-burning furnace used in Mexico was described by E. H. Tays.[3]

Edmands[4] describes similar reverberatory furnaces used for fusions in Rhodesia, and stresses the importance of making an

[1] "A Textbook of Rand Assay Practice," pp. 195–201, 1923.

[2] *Western Chem. Met.*, vol. II, p. 178, 1906; *Eng. Mining Jour.*, vol. 83, p. 80, 1907.

[3] *Trans.* A. I. M. E., *Bull.* p. 2557, October, 1914.

[4] *Jour.* C. M. Met. Soc. S. Africa, vol. XX, p. 180, 1920. *Mining Sci. Press*, vol. 121, p. 452, 1920.

abrupt drop in the roof just beyond the bridge wall. Several types of reverberatory furnace are illustrated in Rand Metallurgical Practice and Rand Assay Practice (Fig. 11).

In these furnaces, the fuel doors are usually on the opposite side from the working doors, as in most coal-fired furnaces, but they can evidently be fired from the end or the front if desired, and oil or other fuel may be substituted. In the Rival furnace, the muffle hearth is immediately over the melting hearth, and both use the same stack.

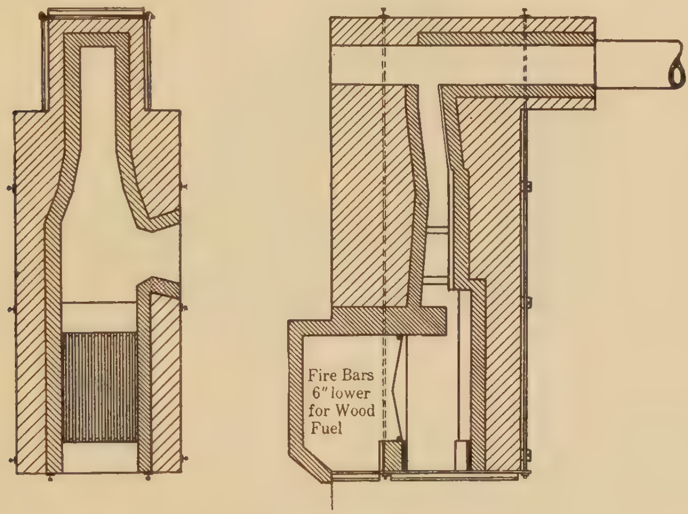

FIG. 11.—Reverberatory assay-furnace. (Scale: 3/32 in. = 1 ft.)

When gas can be obtained of uniformly good quality and at uniform pressure, it is by far the most convenient and desirable fuel, provided the cost is not prohibitively high, as it is readily lighted and controlled, is dustless and almost silent, and the products of combustion give but little trouble. While a considerable proportion of the heat is carried off in the waste gases, this can be reduced to a minimum by proper adjustment of the gas and air supply. When variable in quality and pressure, the advantages of gas are, to a great extent, lost.

Pulverized Coal.—In 1918, the United States Smelting Company[1] of Midvale, Utah, successfully substituted pulverized coal for lump coal in a set of three-muffle furnaces of the type shown in

[1] *Mining Met.* Vol. II, p. 24, December, 1921.

Figs. 3 and 4. A steel bin was hung at the back with its bottom level with the furnace top. The coal is fed from the open bottom of the bin by a variable screw feed made from a 2-in. auger and drops through a ¾-in. hose into a funnel and then into a 3-in. pipe leading into the furnace. This pipe is connected with a No. 2 B. F. Sturtevant fan running at 1,750 r.p.m. which supplies air to three furnaces, each of which consumes about 45 lb. of coal per hour. The fire is easily started with lighted oily waste, and combustion is complete, giving a steady, uniform heat. Most of the dust falls into the ash pit, and a loose brick is kept on the top of each muffle for removing any ash that collects upon it.

A self-contained muffle unit for pulverized coal was formerly built, comprising a single muffle furnace and a McCool ball pulverizer driven by a 2-hp. motor, the rotating mechanism carrying a fan for feeding the pulverized coal and a device for returning the oversize. One of these machines has been in constant use in Victor, Colo., for many years, consuming about 12 lb. of coal per hour.

In establishments where pulverized coal is in use, there is no apparent reason why it should not be used more generally for heating muffle furnaces or fusion furnaces of the reverberatory type; in the latter, the crucibles might require covering to exclude ash. Fine pulverization and ample combustion space are desirable for such relatively small-scale work.

Gasoline-fired Furnaces.—Furnaces of this type are in common use, and for small offices, where the pressure of work is not great, they afford a convenient and cheap method of operation. Gasoline, on account of ease of transportation and great calorific power, is also employed in out-of-the-way districts for extensive daily work. Where coal is reasonably cheap, not above $6.50 per ton, gasoline at about 20 cts. per gallon cannot compete with it in large offices or schools, where the assay furnaces are operated continuously for the greater part of the day.

Figure 12 shows a gasoline-furnace apparatus. The furnace, divided into crucible and muffle compartments, is made of fireclay tiling, bound with sheet iron. It is heated by a brass and copper burner, provided with a generating device. The burners are made in varying sizes to suit different furnaces. The gasoline is stored in a steel tank, of 5 or 10 gal. capacity, provided with an air pump to furnish pressure. A pressure gage is

attached to the tank. Generally, 0.25- to 0.375-in. piping joins the tank and the burner. The burner and piping are connected by a special universal joint, so that the burner can be swung into and out of position. The burner (if the Cary) should fit tightly against the fire-clay ring or boss in the opening of the furnace, so that all the air for the combustion of the gasolene is drawn in

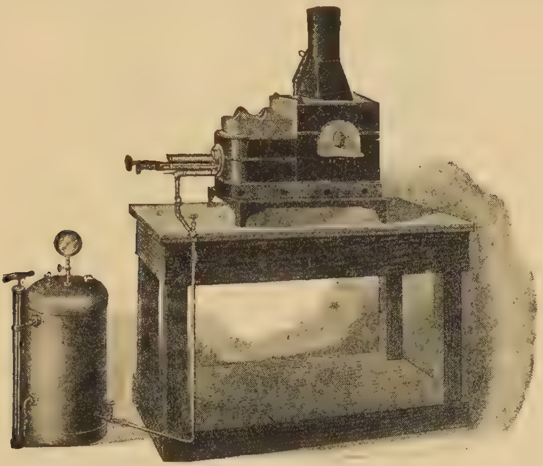

FIG. 12.—Gasoline furnace apparatus.

through the burner tube. To insure tight joints, glue or soap, or shellac, not white or red lead or grease, must be used in the screw connections. The gasoline is fed to the burner under a pressure of 10 to 20 lb., though for special purposes higher pressures are used, up to 50 and 60 lb. per square inch.

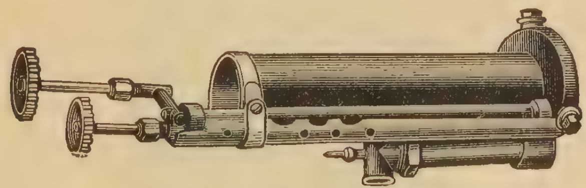

FIG. 13.—The Cary gasoline burner.

Figure 13 shows a detailed view of the Cary burner. The upper valve controls the main gasoline supply, and the lower one controls the generator. The burner is heated by the generator, so that the gasoline issuing from the main needle valve is vaporized and in its passage to the furnace draws in air through the burner tube, the mixture igniting and burning at the mouth

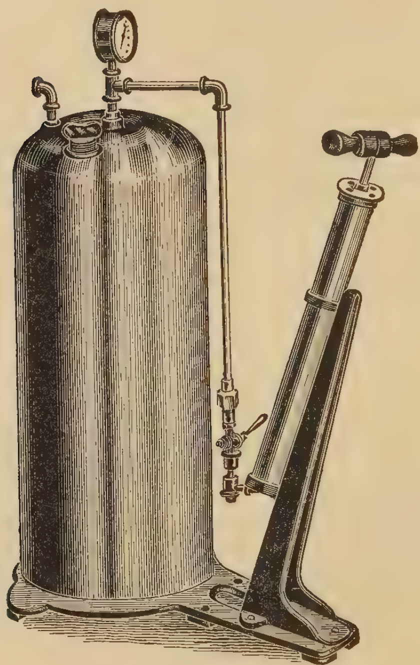

Fig. 14.—Gasoline tank and pump apparatus.

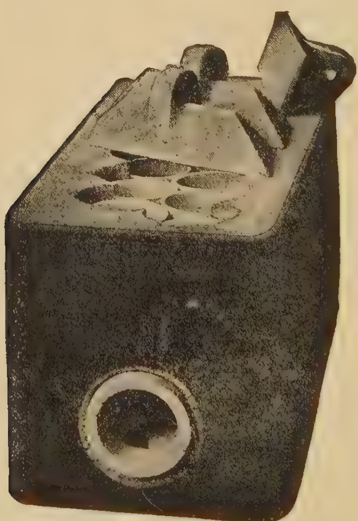

Fig. 15.—Gasoline-burning crucible furnace.

of the burner in the hot furnace. Burners are listed by the diameter of their tubes. Five sizes are made, from 1.25 to 2.25 in., each size varying by 0.25 in.

Figure 14 shows the tank and pump apparatus. It is best to place this at a considerable distance from the furnace, in order to avoid accidental explosions. Figure 15 shows a crucible

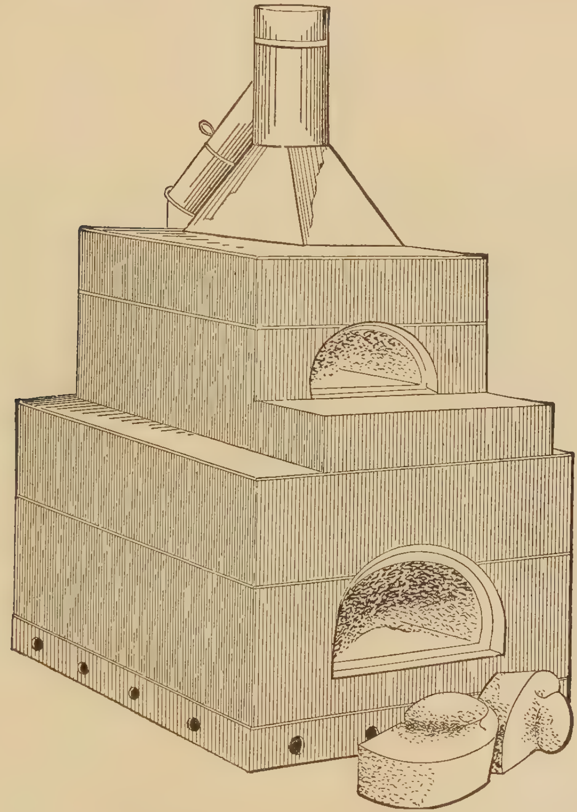

Fig. 16.—Front view of gasoline burning muffle-furnace with muffle-shaft flue.

furnace, and Fig. 16 a large gasoline muffle furnace. A temperature of 1350° C. has been attained in small gasoline furnaces, such as Fig. 15 represents, and 1250° C. in large furnaces, as represented by Fig. 16. By a special construction of furnace, with graphite muffle and heavy insulation against radiation, with good draft (for metallurgical experimentation) temperatures of 1500° to 1530° C., have been attained after 3 hours, with a 2-in. gasoline burner as shown in Fig. 13, with gasoline at a

pressure of 55 lb., and a consumption of 1.53 gal. per hour. A 2-in. Cary burner, under 10 lb. pressure, will consume from 0.65 to 0.75 gal. per hour. A No. 31 Cary combination furnace, holding at a charge in the crucible compartment six 20-g. crucibles and having a muffle 7 by 10.5 by 4.5 in. in size, has a capacity of 10 fusions per hour, including cupellation. With gasoline at 20 cts. per gallon, the cost of fuel per assay is 1.5 cents.

Figure 17 shows the Case burner for gasoline or similar distillate. When in the proper position, it is inverted, *i.e.*, the preheating system is at the top instead of at the bottom, as in the Cary burner. The generator or boss in which the gasoline is vaporized is cast in one piece with the *mixing chamber* which is in

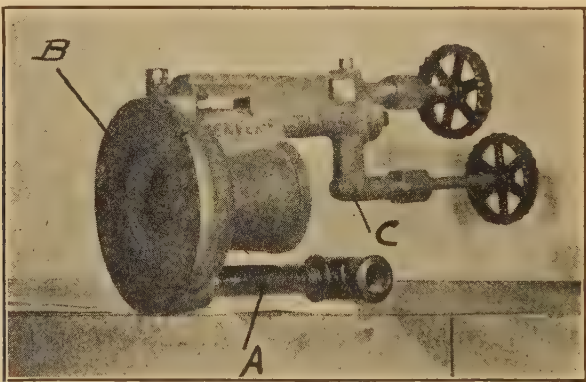

FIG. 17.—Case-burner. *A*, Nipple containing gravel for straining gasoline *B*, generator; *C*, valve.

the form of a truncated cone and very much shorter than in other gasoline burners. The burner is smaller and more compact than the ordinary burner of the same capacity. The fact that it is inverted permits the gas formed from the gasoline in the generator to pass freely upward to the valves. The valves are of special design. Ordinarily, the needle valve is used in burners of this type, that is, a pointed, hard-steel needle works in the circular valve orifice, making an annular opening for the escape of the gas. This annular opening varies in dimensions according to the position of the needle and may be closed completely by screwing the needle up as far as it will go. With use, the tendency of the needle is to enlarge the valve orifice and cause increased consumption of gasoline. The valve of the Case burner is closed by the valve seat's meeting a shoulder

on the valve stem, both planed surfaces. The opening for the flow of gas is annular, as before, but the end of the blunt valve pin does not close the valve. The burner is made of phosphor bronze and operates best under a pressure of from 40 to 50 lb.

When gasoline is used on a larger scale, it is desirable to have a tank of at least 20 to 50 gal. capacity buried in the ground or sunk in a concrete pit and to supply compressed air by a small power pump of the garage type. If this is electrically driven, it may be stopped and started automatically to maintain a constant pressure. Duplicate tanks are still more convenient, as one may

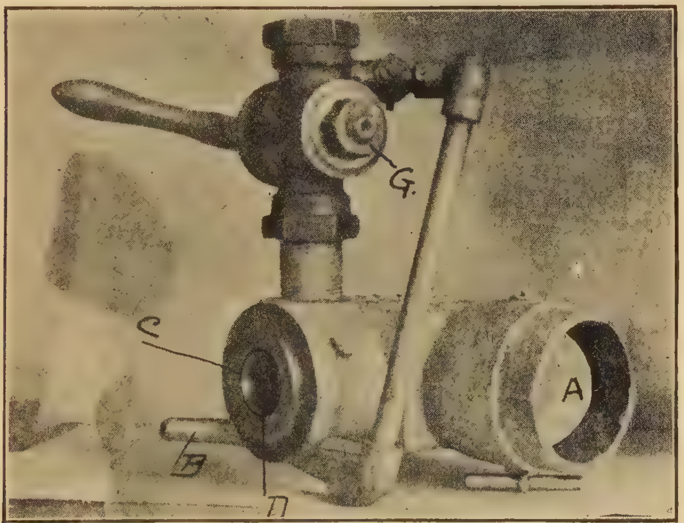

FIG. 18.—Case gas-burner, air furnished by low pressure blower.

be filled while the other is in use. It is convenient to include in the equipment a filter or strainer of wire gauze and a trap to remove small quantities of water which can be drained by a valve or plug. In cold climates, the trapping of water is essential. All gasoline piping should slope so as to drain away from the burners to the reservoir, and there should be an air outlet or release controlled from a point near the burner. Burners and furnaces of many types are now in use with distillate and crude oil sprayed in by a jet of air under low pressure.

Figure 18 shows a gas burner for assay furnaces. The air supply is controlled by the butterfly valve *A*. The gas issues from the circular opening *D* and mixes with the air from the

annular opening C, for combustion. The gas flow is regulated by the cock G. The burner is provided with the pilot tube B to ignite the gas in starting the burner.

Gas Furnaces.—Where gaseous fuel is available, gas-fired furnaces are convenient and cheap of operation. The Reichhelm furnace (American Gas Furnace Company) is frequently used. Air is required at low pressure, and this is mixed with gas in proper

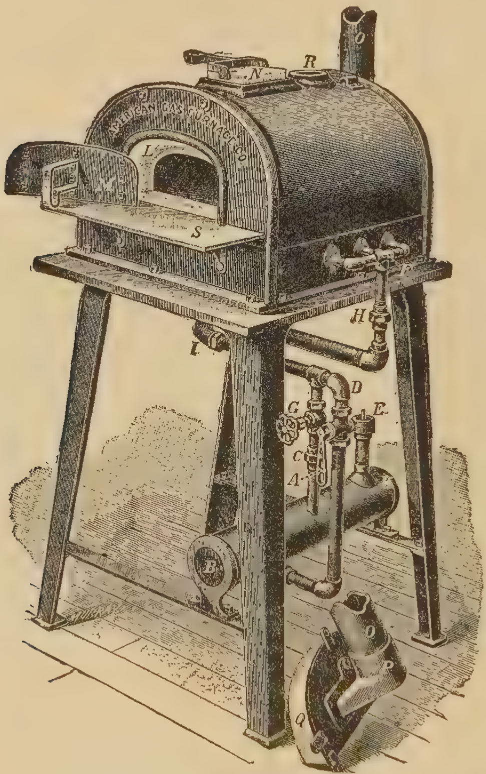

Fig. 19.—Gas-burning muffle-furnace.

proportion before it enters the furnace through the several burners. The No. 2 furnace, with muffle 6.75 by 3.75 by 12 in. is used for cupellation in the U. S. Mint Service; No. 3 has a muffle 11.5 by 5 by 14 in. The muffle draft is produced by a vertical iron pipe O. The proportion of gas to air is controlled by valves. Figure 19 shows the furnace. Gas furnaces permit of close control of heat and are desirable for accurate temperature work. The fuel used can be accurately measured by a suitable meter. English gas furnaces made by Fletcher have a number

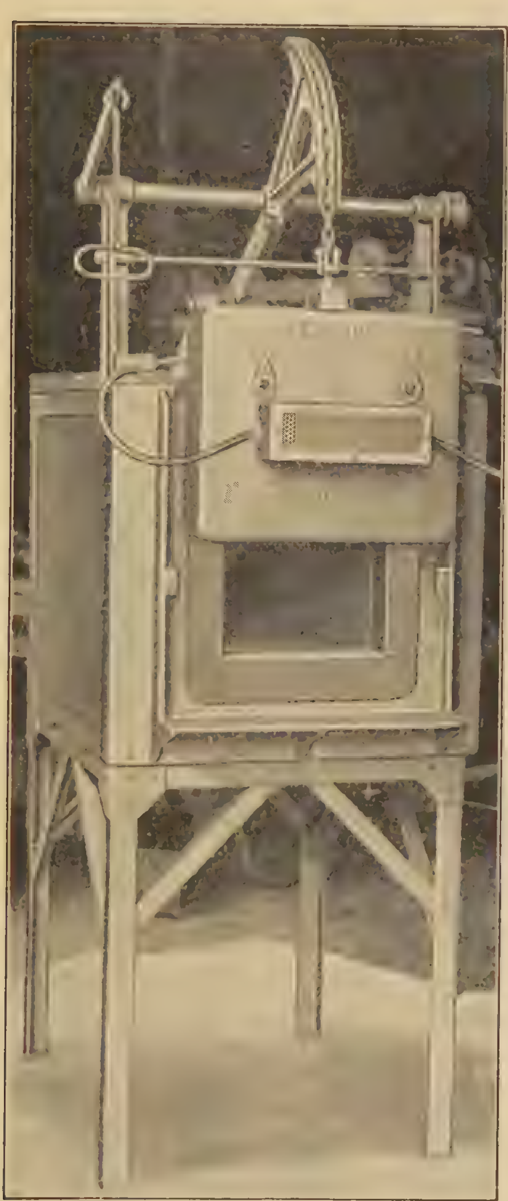

Fig. 20.—Hevi-duty electric muffle-furnace.

of large bunsen burners in a row under the center line of the muffle and the furnace bottom has an open slot to correspond.

Electric Furnaces.—Electricity gives an almost ideal method of heating muffles by means of replaceable resistance units. While comparatively costly considered merely as a source of heat, electricity has a very high degree of efficiency, mainly owing to the absence of gaseous or other by-products to carry off heat, partly due to the compactness of the heating elements, allowing of thorough insulation. Owing to the rather frail character of the earlier electric muffles and the rapid deterioration of the linings in contact with litharge fumes, electricity has been but little used in assay work, except for experimental purposes requiring rigid control. Strongly constructed furnaces are now available and have proved themselves durable and

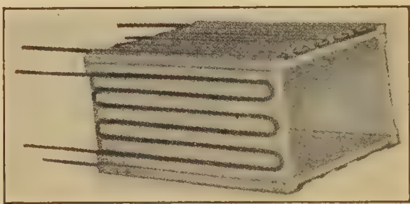

FIG. 21.—Electric heating unit for muffle-furnace.

economical under severe usage. They are clean, noiseless, and readily controllable.

The Hollinger Consolidated Gold Mines, Ltd., of Timmins, Ont., have a battery of six "Hevi-duty" electric furnaces, of which five are in constant use 24 hours a day, making 1,000 fusions and 1,200 cupellations daily, as well as other operations. The muffles are 13.5 by 22 by 8 in., accommodating twenty-four 20-g. crucibles, and the heating elements are return bend coils of 4-gage nichrome wire held in position by replaceable grooved muffle plates. Each furnace has its own transformer and radial switch and a pyrometer. The current required for heating is 11 kw., and the average for running about two-thirds of this. While the first cost is relatively high, the upkeep is low, coils and plates averaging 4 months in life and crucibles having an unusually long life. Damaged coils can be easily repaired by electric welding.

Figure 20 shows a modern Hevi-duty furnace for assay use, and Fig. 21, the type of heating unit used. An assay muffle

furnace in which carborundum rods, called *globar rods*, made by the Globar Company of Niagara Falls, N. Y., are used as resistance units is in use in the assay laboratory of the Missouri School of Mines.[1]

TABLE I.—COMPARATIVE COST OF HEAT

Source	Heat value	Price	B.t u. per dollar	Cost per million B.t.u.
Electricity	1 kw.-hr. = 3,400 B.t.u.	1 ct. per kilowatt-hour	340,000	$ 2.94
		5 cts. per kilowatt-hour	68,000	14.70
Natural gas	1,000 B.t.u. per cubic foot	$1 per 1,000 ft.	1,000,000	1.00
City gas	500 B.t.u. per cubic foot	$2.50 per 1,000 ft.	200,000	5.00
Blau gas	Cylinder of 26.5 lb. said to yield 675,000 B.t.u. Cylinder tare 115 lb.	$6.75 per cylinder including freight	100,000	10.00
Acetylene	Carbide 80 per cent, 6,972 B.t.u. per pound	8 cts. per pound	87,150	11.47
	Carbide 90 per cent, 7,843 B.t.u. per pound	6 cts. per pound	130,700	7.65
Gas-machine gasoline	88° Bé., sp. gr. 0.65 about 22,000 B.t.u. per pound	44 cts. per gallon	270,000	3.70
Gasoline	Sp. gr. 0.75, about 21,000 B.t.u. per pound	20 cts. per gallon	565,000	1.52
Kerosene	Sp. gr. 0.80, about 20,000 B.t.u. per pound	15 cts. per gallon	900,000	1.11
Distillate	Sp. gr. 0.85, about 19,000 B.t.u. per pound	12 cts. per gallon	991,000	1.01
Fuel oil	Sp. gr. 0.90+, about 18,000 B.t.u. per pound	6 cts. per gallon	2,250,000	0.45
Sub-bituminous coal	10,000 B.t.u. per pound	$10 per net ton	2,000,000	0.50
Coal screenings	8,000 B.t.u. per pound	$4 per net ton	4,000,000	0.25
Coke	85 per cent fixed carbon, about 12,500 B.t.u. per pound	$16 per net ton	1,560,000	0.64
Charcoal	Locally burned, about 14,000 B.t.u. per pound	2 cts. per pound	700,000	1.43
Pine wood, air dried	9,000 B.t.u. per dry pound, (about 6,000 B.t.u. air dried)	$6 per cord of about 2,000 lb.	2,000,000	0.50

Tons of 2000 lb. U. S. gallons of 231 cu. in.

The above prices approximate closely to those which have actually been paid at various installations in Western states between 1890 and the present date. At other prices the cost can easily be approximated by proportion.

FURNACE TOOLS

Convenient tools are necessary for the handling of crucibles, scorifiers, and cupels. The features essential in these tools are that they be light, grasp the crucible, etc., firmly, with no danger

[1] CLAYTON, C. Y., *Private Communication.*

of tipping, and take up little room in the furnace. As an illustration of a tool deficient in these qualities and, therefore, undesirable, Fig. 23 is given. This shows a pair of crucible tongs

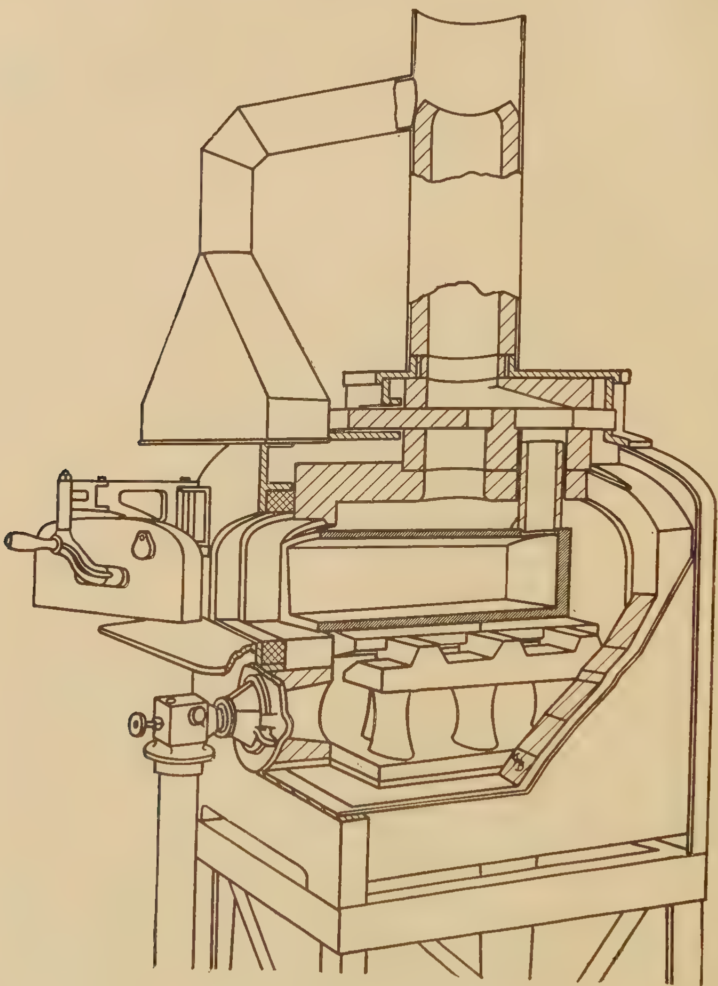

Fig. 22.—Detail of DFC oil-fired assay-furnace.

designed to grasp the body of the crucible. It cannot be handled in a muffle full of crucibles, owing to the space that it takes up in opening. Figure 24 shows the common tools used in the Homestake Assay Laboratory.

For large offices where much work must be quickly accomplished, special forms of tools may be used (Fig. 25).

Figure 26 shows a device to charge 30 cupels[1] at one time. It comprises a top sliding plate with openings corresponding exactly to the position of the cupels. The openings in the lower plate correspond to those of the upper one; the plate, however, rests on two adjacent sides extended downward at right angles to the plate and to each other, thus forming two closed sides of the instrument, one at the front and the other at the right-hand side. The height of these sides is such that when resting on the bottom of the muffle the bottom plate will be some distance above the cupels, and by a slight pull forward and a push to the left with the handle of the instrument the set of cupels will be perfectly alined in both directions and the apertures in

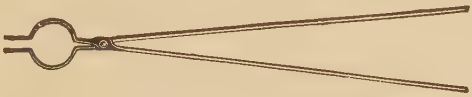

Fig. 23.—Crucible tongs. Undesirable model.

the lower plate will exactly cover the tops of the cupels. The lead buttons are placed in the apertures of the upper plate and rest on the lower plate before introducing the instrument into the furnace, and when it is placed over the cupels, which have been properly alined in the muffle, the upper plate is pushed forward to a stop point, bringing the apertures of the two plates into register, thus causing the lead buttons to drop down into the cupels. The handle of the upper plate runs through guides fixed to the handle of the lower plate; both handles are connected with a spring, which acts as a brake when the upper plate is pushed forward to drop the buttons and also serves to bring it back into its original position, in which the buttons cannot drop through the apertures in the lower plate.

Molds.—Figure 27 shows machined cast-iron molds to receive the molten fusions. The sharp, cone-shaped mold is preferable to the shallow, hemispherical type, as the lead buttons are then sharp and well defined and separate easily from the slag. The mold is best made with a screw handle so as to be easily repaired in case of breakage. The inner surface of the molds should be machined smooth, to permit the ready separation of slag and

[1] Keller, Edward, "Labor-saving Appliances in the Works Laboratory," *Trans.* A. I. M. E., vol. XXXVI, p. 3; *Bull.* 44, p. 633, August, 1910.

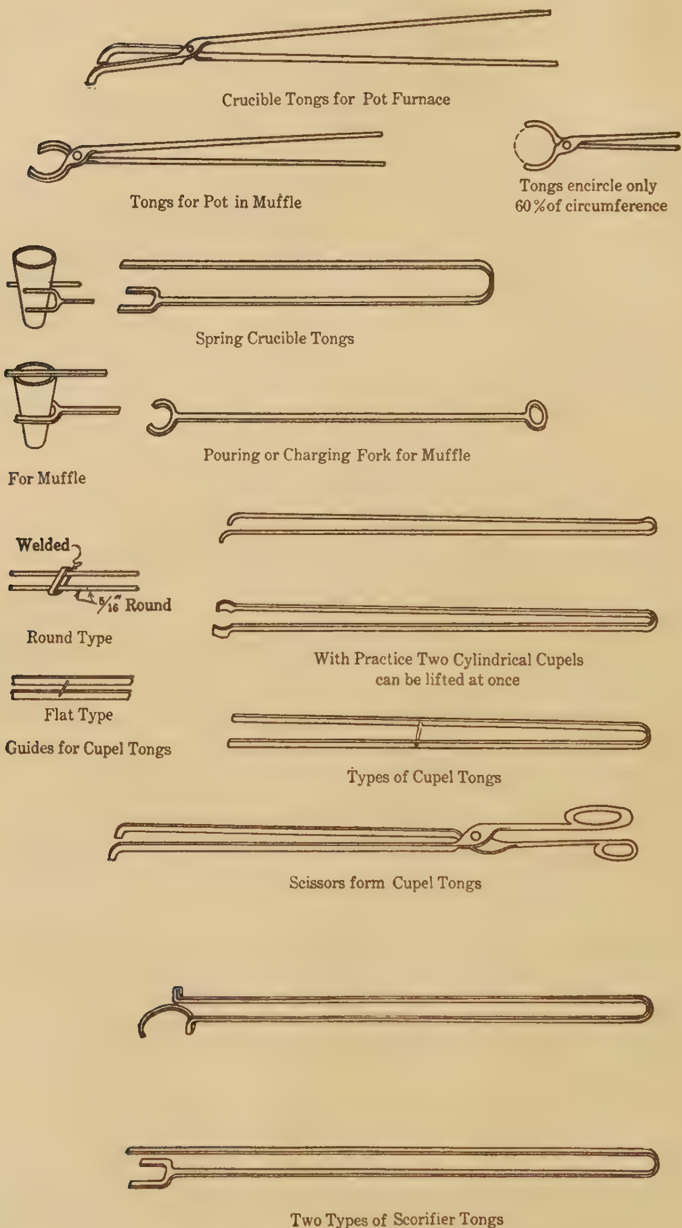

FIG. 24.—Assay tools used in the Homestake assay-laboratory.

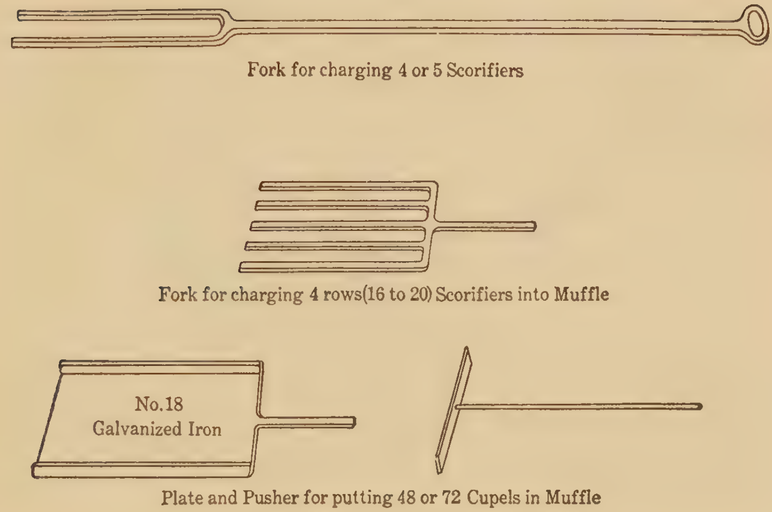

FIG. 25.—Assay tools for multiple-work.

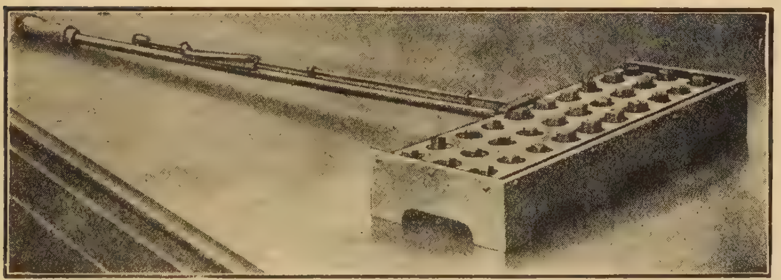

FIG. 26.—Cupel charging device. (*Keller.*)

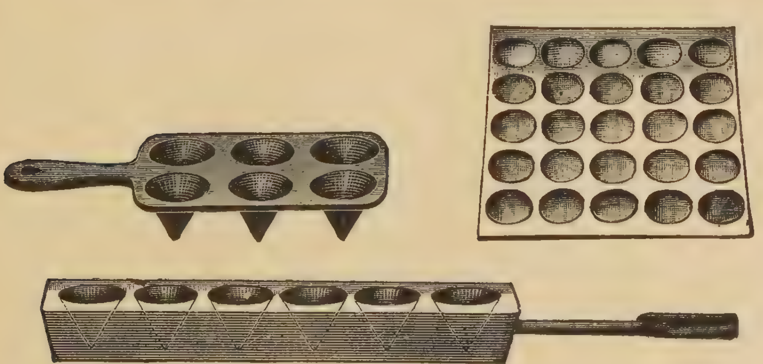

FIG. 27.—Pouring molds.

lead button from the mold. For scorification fusions, smaller molds are often used.

For the transfer of cupels to the parting room, iron cupel trays, as illustrated in Fig. 28, are used. The handle is removable, and one handle serves for a number of trays. For the annealing of

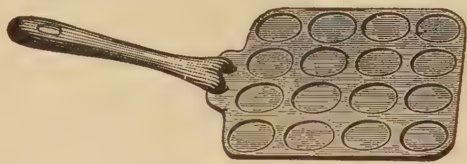

FIG. 28.—Cupel tray.

gold beads, or cornets, fire-clay trays as shown in Fig. 29 are employed. Fire clay, however, is very easily broken, and more satisfactory trays are made of sheet iron and heavy asbestos board.

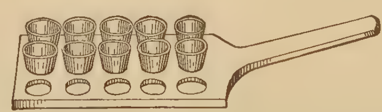

FIG. 29.—Fire-clay annealing-cup tray.

Crucibles and Scorifiers.—Fire-clay crucibles are largely used in the United States, and fire-clay ware for assay purposes is made, to a large extent, in some of the Western states. Following is the analysis of a Colorado crucible clay:[1]

	Raw, per cent	Burnt, per cent
Loss on ignition	10.14	
Alumina	15.09	16.81
Silica	71.81	79.90
Ferric oxide	1.75	1.95
Lime	0.14	0.15
Magnesia	0.05	0.06
Alkalies	1.02	1.13

Table II gives the composition of assay crucibles. Most of the analyses were made in the Homestake Mine Laboratories.

[1] ORTON, EDWARD, "Assay Crucibles, Their Clays," *Trans.* Am. Ceramic Soc., vol. X, p. 484, 1908.

The crucibles are rated by *gram* capacity, that is, by the number of grams of ore with the proper amount of fluxes necessary for fusion which the crucible will hold. The chief sizes are 5, 10, 12, 15, 20, 30, 35, and 40 g.; of these the 20- and 30-g. sizes are mostly used, the 20-g. crucible for the 0.5-assay-ton and the 30-g. for the 1-assay-ton fusions. Figure 30 shows the various shapes employed. Imported Hessian triangular crucibles and sand crucibles are also used but in small quantities.

Imported Battersea clay crucibles give good satisfaction and are used by some of the large assay offices in preference to domestic fire-clay goods, for the reason that their quality is generally uniform and that they last for a larger number of fusions than the poorer grade of domestic goods which are sometimes sold. The highest grade of domestic material is, however, in most cases, to be preferred as being fully as long lived and cheaper.

TABLE II.—ANALYSES OF ASSAY CRUCIBLES

<table>
<tr><th></th><th>Silica</th><th>Alumina</th><th>Iron oxide</th><th>Magnesia</th><th>Lime</th><th>Ignition</th></tr>
<tr><td>1. Beaufay, Paris</td><td>64.6</td><td>34.4</td><td>1.0</td><td></td><td></td><td></td></tr>
<tr><td>2. Deleuil, Paris</td><td>72.3</td><td>19.5</td><td>3.9</td><td></td><td></td><td></td></tr>
<tr><td>3. Hessian sand; half Gross-Almerode clay, half sand</td><td>70.9</td><td>24.8</td><td>3.8</td><td></td><td></td><td></td></tr>
<tr><td>4. Gross-Almerode</td><td>72.9</td><td>24.75</td><td>2.15</td><td colspan="2">0.03</td><td>0.17</td></tr>
<tr><td>5. New Jersey, 1918</td><td>57.06</td><td>38.50</td><td>2.24</td><td>0.72</td><td>0.56</td><td>1.08</td></tr>
<tr><td>6. New Jersey, 1924</td><td>78.40</td><td>17.82</td><td>1.12</td><td>0.50</td><td>0.64</td><td>1.04</td></tr>
<tr><td>7. Utah, 1925</td><td>75.94</td><td>21.38</td><td>1.28</td><td>0.70</td><td>0.90</td><td>0.16</td></tr>
<tr><td>8. Colorado, old soft</td><td>65.42</td><td colspan="2">33.82</td><td colspan="2">0.74</td><td></td></tr>
<tr><td>9. Colorado, hard special, 1909</td><td>71.1</td><td colspan="2">26.4</td><td colspan="2">2.5</td><td></td></tr>
<tr><td>10. Colorado, 1919</td><td>69.25</td><td>26.9</td><td>2.0</td><td colspan="2">1.85</td><td></td></tr>
<tr><td>11. Colorado, 1926</td><td>68.80</td><td>28.80</td><td>1.36</td><td>0.64</td><td>0.56</td><td>0.0</td></tr>
<tr><td>12. Battersea H, 1905</td><td>71.02</td><td colspan="2">27.02</td><td colspan="2">1.96</td><td></td></tr>
<tr><td>13. Battersea S, 1905</td><td>72.14</td><td colspan="2">25.90</td><td colspan="2">1.96</td><td></td></tr>
<tr><td>14. Battersea Special soft, 1909</td><td>71.64</td><td colspan="2">26.10</td><td colspan="2">2.26</td><td></td></tr>
<tr><td>15. Juleff's Cornish pot, Redruth</td><td>72.39</td><td>25.32</td><td>1.07</td><td>Trace</td><td>0.38</td><td>(K_2O 1.14)</td></tr>
</table>

1, 2, 3—Analyses by Berthier, 1834, quoted by Percy.
4 —Analysis by J. Loevy, Johannisberg.
15 —Analysis by A. Dick, quoted by Percy.
All others by Homestake Mining Company.

FIG. 30.—Fire-clay crucibles.

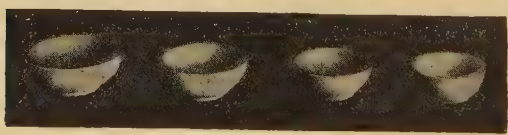

FIG. 31.—Scorifiers.

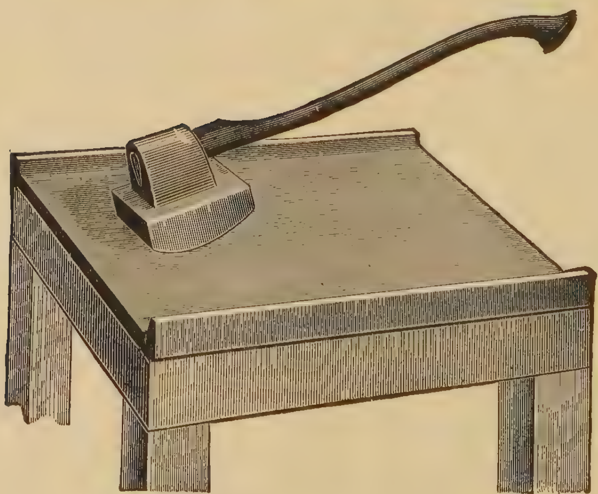

FIG. 32.—Buck board and muller.

The special mixture of clays and their treatment for crucible manufacture are generally considered a trade secret, jealously guarded, and little information concerning the subject is available.

Scorifiers are made of the same clays as the crucibles and are designated in size by their outside diameters; 1.5-, 2-, 2.5-, and 3.5-in. sizes are made. These will hold a volume of 15, 25, 37, and 100 cc., respectively. The 2.5-in. scorifier is the one commonly used. Figure 31 shows the ordinary type of scorifiers.

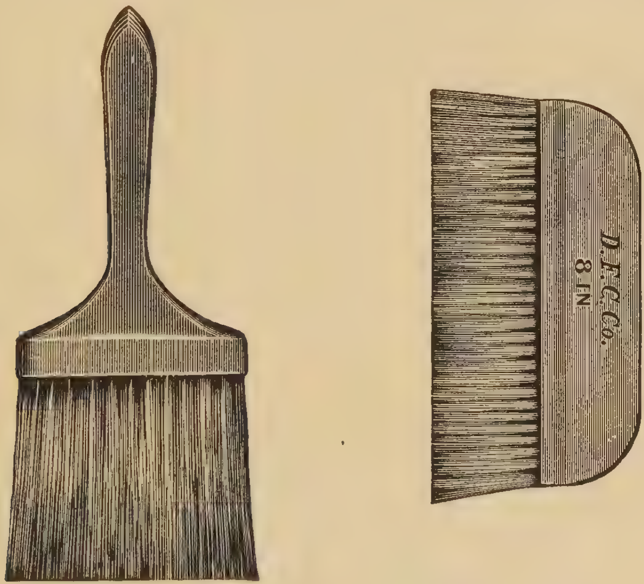

Fig. 33.—Buck board brushes.

Roasting dishes are shallow fire-clay dishes similar to scorifiers but not so thick. They are rated by their diameters, the common sizes being 3, 4, 5, and 6 in.

Figure 32 shows the ordinary buckboard and muller, and Fig. 33 buckboard brushes. For the description of other minor tools and apparatus, as screens, pliers, and crushing and grinding machinery, necessary to the assay laboratory, the reader is referred to the voluminous and well-illustrated catalogues of the assay supply houses. Balances, weights, sampling tools, cupels, parting devices, etc., are discussed in their respective chapters.

CHAPTER III

REAGENTS AND ASSAY OF REAGENTS

Reagents

The solid and liquid reagents commonly used in assaying are described in this chapter.

Solid Reagents. 1. *Sodium Carbonate* (Soda Ash, Anhydrous Na_2CO_3; mol. wt. 106.0; Na_2O, 58.5; CO_2, 41.5 per cent). Next to litharge this is the most important flux in the fire assay; it is also much the cheapest. It melts without appreciable decomposition at 853° C. In the presence of silica it reacts to form sodium silicates and gives off gaseous carbon dioxide for example:

$$\underset{62}{Na_2CO_3} + \underset{60.4}{SiO_2} = Na_2SiO_3 + CO_2$$

These silicates are very fusible and dissolve other oxides to form complex silicates. In a similar way, it reacts to form aluminates. It also readily forms sulphides and sulphates. Thus, with galena it forms a mixed sulphide, part of the lead being reduced to metal; if metallic iron is also present, all the lead is reduced and a fusible mixed iron-sodium sulphide is formed. The essential part of the reagent is the base Na_2O, its effect depending on the ease with which it is decomposed with loss of CO_2. Commercial soda ash contains very little impurity; the dense variety should be purchased in barrels, which usually contain about 350 lb., and not in sacks, and should be kept in a dry place. In a moist atmosphere, it slowly absorbs water and becomes more or less caked. Several crystalline varieties of sodium carbonate are sold which contain water of crystallization; washing soda, for instance, is $Na_2CO_3.10H_2O$.

Sodium Bicarbonate ($NaHCO_3$; mol. wt. 84.008; Na_2O, 36.9; CO_2, 52.4; H_2O, 10.7 per cent).—This is the "cooking soda" of the grocery stores and is sometimes used as a flux in place of soda ash, especially in the United States, although it is more expensive and less efficient. Its one advantage is that it has less

tendency to absorb moisture in a damp atmosphere. Its main disadvantage is that it gives off a volume of gas three times as great per unit of Na_2O as the normal carbonate, all the water and half the carbon dioxide being expelled at a rather low temperature, leaving Na_2CO_3: this evolution of gas often causes serious loss of dust from the assay charge; it also cools the mixture and delays fusion. One gram Na_2O requires 1.71 g. Na_2CO_3 yielding about 0.19 l. CO_2 gas as measured at room temperature at sea level. One gram Na_2O requires 2.71 g. $NaHCO_3$, yielding about 0.57 l. CO_2 and water vapor. One gram Na_2O is equivalent to the 1.52 g. K_2O obtained from 2.23 g. potassium carbonate K_2CO_3, also yielding 0.19 l. CO_2. At about 300° C., the volume of gas evolved is doubled, and at about 600° it is trebled, while at any considerable elevation it is increased in inverse proportion to the barometric pressure. It is evident that a flux containing 20 g. of soda ash, or 30 g. of bicarbonate, gives off a large volume of gas which it is desirable to reduce to a minimum.

TABLE III.—REAGENTS COMMONLY USED IN ASSAYING

Name	Chemical formula	Name	Chemical formula
Solid:			
1. Sodium carbonate...	Na_2CO_3	17. Proof silver........	Ag
2. Borax glass.........	$Na_2B_4O_7$	18. Potassium nitrate..	KNO_3
3. Fluor spar..........	CaF_2	19. Sodium chloride....	NaCl
4. Lime.........	CaO	20. Ammonium chloride	NH_4Cl
5. Potassium acid tartrate.	$HKC_4H_4O_6$	21. Potassium iodide...	KI
6. Carbon	C	22. Oxalic acid.........	$H_2C_2O_4$
7. Flour..............		23. Formic acid........	HCO_2H
8. Stannous chloride...	$SnCl_2$	24. Ferrous sulphate...	$FeSO_4 \cdot 7H_2O$
9. Thiocyanates.......	KCNS, NH_4CNS	25. Sulphur dioxide....	SO_2
10. Sodium cyanide.....	NaCN	*Liquid:*	
11. Zinc dust...........	Zn	1. Nitric acid.........	HNO_3
12. Iron...............	Fe	2. Hydrochloric acid..	HCl
13. Sulphur............	S	3. Sulphuric acid......	H_2SO_4
14. Litharge...........	PbO	4. Ammonia..........	NH_3
15. Lead...............	Pb	5. Aqua regia.........	
16. Silver foil..........	Ag		

Potassium carbonate (K_2CO_3; mol. wt. 138.2) is sometimes used in place of sodium carbonate, or partly replacing it. It is

much more expensive, usually impure, and deliquesces in any but the driest atmosphere. It melts at about 885° C. It is now rarely used excepting in the lead assay, its only advantage being that an admixture with sodium carbonate lowers the melting point of the mixture to about 690° C.

2. *Borax Glass* (Fused Anhydrous Sodium Biborate, $Na_2B_4O_7$; mol. wt. 201.28; Na_2O, 30.8; B_2O_3, 69.2 Per Cent, m.p. 742° C.).—Borax is essentially an acid flux and when melted dissolves most metallic oxides readily, including FeO, Al_2O_3, Cr_2O_3, and the alkaline earths. It can also dissolve a considerable proportion of silica. It is, therefore, an excellent flux for such material as clay, slate, or shale, for limestone and magnesite, and manganese or iron ore. Moderate additions of borax lower markedly the melting point of many siliceous slags, but a too large proportion gives increased viscosity.

Crystallized Borax ($Na_2B_4O_7.10H_2O$ contains Borax 52.77, Water 47.23 per cent).—It is usually sold in powdered form, costing about half as much as borax glass. Boric anhydride (B_2O_3) is produced by heating boric acid (H_3BO_3). When added to fluxes or slags containing sodium, it produces the same effect as borax.

In fluxing ores containing zinc, it is to be noted that boric oxide, either alone or mixed with half its weight of borax, will flux zinc oxide into a very fluid slag, which, however, corrodes clay crucibles.

The use of much borax gives rise to hard, stony slags, very tough, from which the lead button separates with difficulty. Often a film of lead will adhere to the slags, causing mechanical loss. Slags containing much borax will often fly to pieces suddenly, especially if touched with a sharp instrument when cooling.[1] This is due to devitrification of amorphous glassy borates and the formation of definite crystallized borates.

3. *Fluor Spar* (Calcium Fluoride CaF_2; mol. wt. 78, m.p. 1380° C.).—Fluor spar when fused is thinly fluid. The greater part of it remains undecomposed and its lime cannot be considered as available for fluxing silica. Slags containing it often have a stony appearance. Owing to its fluidity, it has the property, shared to some extent by soda and litharge, of holding unfused particles in suspension, still giving a fluid slag. It fluxes calcium sulphate and barium sulphate but is not much used. Commer-

[1] Clennell, E., *Eng. Mining Jour.*, vol. LXXXVII, p. 696.

cial sodium fluoride (m.p. about 980° C.) may be substituted. Fluor spar often contains a little galena and, hence, a little silver and should always be tested for silver.

4. *Lime.*—Lime may be used either as the carbonate, oxide, or hydroxide; the former is converted into oxide at 800° C. and above. While highly infusible (1900° C.), it makes with silica good slags for ores. Magnesia (MgO, m.p. 2203° C.) acts in a similar way. Calcium hydroxide ($Ca(OH)_2$) is soluble in 800 parts of water and readily soluble in presence of sugar.

5. *Potassium Acid Tartrate* ($HKC_4H_4O_6$).—Potassium acid tartrate is crystalline and may be used as a reducing agent for litharge; when heated it reacts thus:

$$2HKC_4H_4O_6 = K_2O + 5H_2O + 6CO + 2C$$

the CO and C giving the reducing effect, while the K_2O acts as a basic flux. Argol is an impure variety, usually red or purplish, which separates in the process of making wine from grapes and is often used as a reducing agent; its composition and efficiency vary somewhat.

6. *Carbon.*—Powdered wood charcoal is an impure carbon containing a little ash and may be used as a reducing agent for litharge. Coke or anthracite dust may be used similarly; they often contain a good deal of ash.

7. *Flour.*—Flour is often used as a reducing agent for litharge and is one of the cheapest and most convenient; corn meal and other flours act in the same way as wheat flour. Other organic reducing agents available are sugar, fine sawdust, starch, and sodium or potassium ferrocyanide; none of these is preferable to flour.

8. *Stannous Chloride.*—Stannous chloride ($SnCl_2$) in solution reduces mercuric salts to mercurous and (if added in sufficient quantity) finally reduces all mercury salts to metal. It reduces gold solutions to metal, in some cases forming "purple of Cassius" which contains colloidal gold and stannic hydroxide.

9. *Thiocyanates.*—Thiocyanates (or sulphocyanides, KCNS, NH_4CNS) precipitate silver as AgCNS and copper (from cuprous solution) as CuCNS; they also give a characteristic color with solutions of ferric salts and with gold.

10. *Sodium Cyanide* (NaCN, mol. wt. 49; m.p. 562° C).—Sodium cyanide acts as a reducing agent in the fused state, deoxidizing or desulphurizing such compounds as tin oxide or

lead sulphide and yielding the fused metal, while more or less sodium cyanate or thiocyanate remains in the slag.

$$2NaCN + SnO_2 = Sn + 2NaCNO$$
$$NaCN + PbS = Pb + NaCNS$$

Potassium cyanide (KCN, mol. wt. 65; m.p. 622° C.) acts in exactly the same manner. Each is extremely poisonous and when crushing them great care must be taken to avoid inhaling the dust. The mortar used should be covered with a cloth during the operation. Various mixtures of sodium cyanide with other sodium salts are sold as "98 per cent KCN" and are equivalent to 98 per cent KCN in cyanogen content and reducing effect; the impurities are sometimes objectionable, especially sulphide. "Sodium cyanide 98 per cent" is the purest commercial cyanide in the market. A mixture of two-thirds potassium cyanide and one-third sodium cyanide melts at about 500° C.

Alkaline cyanides in solution slowly dissolve metallic gold and silver and readily dissolve most gold and silver compounds (AgCl, AgBr, AgI, AgCN, AgCNS, and less readily Ag_2S), forming soluble $NaAu(CN)_2$ and $NaAg(CN)_2$, and copper compounds with formation of similar double cyanides. From these solutions careful neutralization with acid usually precipitates cyanides or less soluble compounds, such as AgCN, AgI, CuCN, or CuCl, etc.

11. *Zinc Dust.*—Zinc dust (metallic zinc with a small percentage of zinc oxide) is a general reducing agent when agitated with solutions; it precipitates copper, silver, gold, mercury, tin, and all the less positive metals from their salts and reduces ferric to ferrous salts, etc. The first four metals mentioned are precipitated from double cyanide solutions as well as from chlorides, nitrates, etc. Very finely divided zinc dust is now obtainable practically free from lead, cadmium, and iron.

12. *Iron.*—Metallic iron in the form of wire, filings, "crushed steel," or nails of various sizes reduces copper, mercury, and the precious metals from solutions of their salts but not from double cyanides. It also reduces stannic to stannous chloride. Heated in contact with mercuric sulphide or silver chloride it reduces the metal and also reduces lead from molten slags containing it. In the fire assay of gold and silver ores, iron combines with sulphur of sulphides to form a matte (FeS) or, in the presence of alkali, a mixed sulphide such as $Na_2S.FeS$. It may be used in

the form of large nails, which must be removed before pouring, but in many cases it is more convenient to use small wire nails or brads, ¾ to 1 in. long, cut from No. 18 or No. 20 steel wire. These are completely dissolved in the charge, by combination either with sulphur from the ore or with oxygen from the litharge. They may be weighed or counted out and placed at the top of a crucible charge. The word *penny* in tenpenny, etc., referring to nails, is a corruption of pound and indicates the number of pounds per thousand nails of a given length, when cut from plate; the present wire nails are much lighter.

WIRE NAILS

Size	Approximate length, inches	Approximate weight, grams
10	3	5 to 7
16	3.5	10
20	4	16
30	4.5	18
40	5	25
60	6	40

For the reduction of mercury from cinnabar, iron filings or fine turnings may be used if carefully cleaned, or the more expensive forms of "diamond crushed steel" or "reduced iron."

13. *Sulphur.*—Sulphur, either in the form of "flowers of sulphur" or ground stick, is sometimes used as a reducing agent in the fire assay. It is useful in the case of oxidized copper ores or metallic copper, to combine with copper and keep it out of the lead button.

14. *Litharge.*—Litharge (Lead Oxide, PbO containing 92.83 per cent Lead) is an indispensable reagent in the fire assay of gold and silver. Primarily, it is used to yield, by reduction, a copious shower of minute globules of lead, which alloy with and collect the particles of gold and silver, sinking with them to form a button which on cooling solidifies and can be separated from the barren slag. Any litharge not thus reduced remains in the slag, usually as a silicate or a plumbite, and acts as a valuable flux for silica and other constituents of the ore. Litharge is now obtainable containing a mere trace of silver.

Red lead (approximating Pb_3O_4 with 90.3 per cent Pb) contains more oxygen than litharge but may be used in the same manner, making allowance for the increased oxygen by adding 30 per cent more reducing agent with siliceous ores. It is specified in the flux formulas of many English assayers, but there is no advantage in its use.

15. *Lead.*—Lead for assay purposes should be as nearly free from silver as possible and also free from bismuth. It may be made, if necessary, by reducing litharge with charcoal in a clean crucible at low temperature.

Lead foil may be rolled out in the laboratory rolls to any desired thickness, but it is now purchasable in suitable condition for use in the bullion assay, in rolls of 5 lb. each, 3 in. wide, and practically free from silver. A convenient thickness is about 0.005 in., when 1 sq. in. weighs almost exactly 1 g.

Granulated lead or "test lead" for scorification can be purchased in bags of 50 lb. It can be made by heating lead just above the melting point, pouring it into a wooden box, and shaking violently with a horizontal motion just as it is on the point of solidifying. Much of the lead will be found as a coarse powder; this is separated by a 40-mesh sieve, and the coarser portion is remelted and shaken again.

A square or rectangular box of ¾-in. hardwood, about 18 in. square by 6 in. deep, answers well for the shaker. When larger quantities are to be prepared, the box should be suspended by two or three light rods or chains.

16. *Silver Foil.*—Silver foil for inquarting ore assays should be as pure as possible.

17. *Proof Silver.*—Proof silver and proof gold for the bullion assay should be of the highest purity. These may be purchased from the United States mint at Philadelphia or may be prepared by electrolysis or other means.

18. *Potassium Nitrate.*—Potassium nitrate (KNO_3, mol. wt. 101; m.p. 339° C.) is used as an oxidizing agent. With metallic lead it acts approximately as follows:

$$7Pb + 6KNO_3 = 7PbO + 3K_2O + 3N_2 + 4O_2$$

the K_2O formed then plays the part of a basic flux. It is frequently used in the fire assay to oxidize impurities in the charge, such as sulphur and arsenic. It is often called *niter* or *saltpeter.*

Sodium nitrate ($NaNO_3$, mol. wt. 85; m.p. 310° C.) may be used in place of niter and is more effective as well as cheaper; it has the disadvantage of absorbing moisture from the atmosphere and of deliquescing in some climates. In damp climates it is desirable to dry ordinary niter at 100° C. before use.

19. *Sodium Chloride.*—Sodium chloride (common salt, NaCl, mol. wt. 58.45; m.p. about 800° C.) is sometimes used as a cover for fusions; it is thinly fluid and is not decomposed during the fusion. In solution it is used as a precipitant for silver. It vaporizes readily above 1000° to 1100° C.

20. *Ammonium Chloride.*—Ammonium chloride (NH_4Cl, mol. wt. 54.5) precipitates silver as AgCl, and a strong (20 per cent) solution precipitates platinum as a double chloride ($(NH_4)_2PtCl_6$, ammonium chloroplatinate), which is less soluble than K_2PtCl_6.

21. *Potassium Iodide.*—Potassium iodide (KI) precipitates silver as KI, palladium as PdI_2, and gives more or less characteristic colors with solutions of some other platinoid metals. It liberates iodine with oxidizing agents such as ferric chloride, cupric salts, and auric chloride.

22. *Oxalic Acid.*—Oxalic acid ($H_2C_2O_4.2H_2O$, mol. wt. 126.1), a weak reducing agent in solution, precipitates gold from warm acid solutions without affecting other heavy metals. Ammonium oxalate ($(NH_4)_2C_2O_4.H_2O$, mol. wt. 124.2) with HCl acts in the same way by liberating $H_2C_2O_4$.

23. *Formic Acid.*—Formic acid (HCO_2H), or a formate plus HCl, reduces gold and some of the platinum metals from solution.

24. *Ferrous Sulphate.*—Ferrous sulphate ($FeSO_4.7H_2O$) and other ferrous salts act as reducing agents, precipitating gold from solution.

25. *Sulphur Dioxide.*—Sulphur dioxide (SO_2) in water solution is equivalent to sulphurous acid ($H_2S_2O_3$); it reduces ferric, cupric, and platinic salts to a lower stage of oxidation and precipitates gold from chloride solutions. Sodium sulphite (Na_2SO_3) with HCl reacts in the same way.

Liquid Reagents. 1. *Nitric Acid* (HNO_3, mol. wt. 63.016).—Solvent (concentrated or dilute) for silver, mercury, copper, and most other metals. Palladium is slowly dissolved; palladium and platinum alloyed with much silver are both dissolved by it. Heated in concentrated form it is an oxidizing agent for sulphur, etc. As a rule, it does not evolve hydrogen when dissolving

metals, but a further quantity of HNO_3 is reduced to NO, N_2O, or other oxides of nitrogen.

2. *Hydrochloric Acid* (HCl, mol. wt. 36.465, in Aqueous Solution).—Solvent for most of the more positive metals, and precipitant for silver as AgCl. It is often convenient for removing metallic iron, zinc, or aluminum from metallurgical products preliminary to assay and occasionally for removing carbonates of calcium and magnesium.

3. *Sulphuric Acid* (H_2SO_4, mol. wt. 98.08).—When hot and concentrated, sulphuric acid is a solvent for metallic silver, copper, and mercury; also for spongy palladium; in dissolving them it is partly reduced to SO_2 and other products. When cold or considerably diluted, it scarcely affects these metals but readily dissolves metallic iron or zinc, evolving hydrogen. It precipitates lead and barium from solutions as $PbSO_4$ and $BaSO_4$ and calcium from solutions which are not too dilute as $CaSO_4.2H_2O$.

4. *Ammonia* (NH_3, mol. wt. 17.032, in Aqueous Solution; Strong Solution is Equivalent to a Solution of Ammonium Hydroxide, NH_4OH, mol. wt. 35.048).—It acts as a strong base and is used to neutralize acids and as a solvent for silver chloride and most other silver salts (not for AgI or Ag_2S). It precipitates most metals from their solutions as hydroxides, many of them (Cu, Ag, Zn, Ni, Co) being soluble in excess or in the ammonium salts formed, in some cases as complex metallammonium compounds.

5. *Aqua Regia.*—This is a solvent for gold, palladium, platinum, and attacks other platinum metals less readily; it attacks silver superficially until the metal becomes coated with insoluble chloride; it dissolves most other metals readily but has no advantages as a solvent over other acids. It oxidizes sulphur to SO_3 (H_2SO_4), Fe'' to Fe''', Hg' to Hg'', etc. The solvent or oxidizing effect is essentially due to free chlorine or nitrosyl chloride (NOCl).

Aqua regia is preferably mixed when required for use, but if cooled at once and kept cold it may be retained for a considerable time. As a rule, the best proportion is 1 volume of strong nitric to 3 or 4 volumes of strong hydrochloric acid. It is generally desirable to use too much hydrochloric rather than too little. By several evaporations with some additional hydrochloric acid, the nitrogen compounds may be completely expelled.

These strong acids should be stored in a cool place. They and ammonia may be purchased in carboys, which hold approximately 100 lb. of water (12 U. S. gal. or 10 imperial gal.), or in glass-stoppered bottles, known as *Winchester quarts*, which hold 2.5 l. (about 9 lb. sulphuric, 7 lb. nitric, 5 lb. hydrochloric acid, and 4 lb. ammonia). Eight such bottles are usually shipped in a barrel and 6, or some multiple of 12, in a case; cases and carboys are returnable. Certain restrictions are imposed on their transportation by railroads and other carriers, and in remote places the hazard and cost of transportation makes them extremely expensive, so that it is a matter of economy to adopt methods of assay which minimize the quantities of liquid reagents in particular, as well as fluxes and fuel.

Table IV.—Data on Liquid Reagents

Reagent	Specific gravity	Percentage by weight	1 cc. contains approximately	Approximate normality
Nitric acid (HNO_3, mol. wt. 63.016).	1.42 1.40	70	1 g. HNO_3	11
Sulphuric acid (H_2SO_4, mol. wt. 98.08).	1.84	95	1.75 g. H_2SO_4	36
	1.835	93	1.7 g. H_2SO_4	
Hydrochloric acid (HCl, mol. wt. 36.465).	1.20	40	0.48 g. HCl	13
	1.18	35.5	0.42 g. HCl	11.5
	1.10	20	0.22 g. HCl	6
	1.09	18	0.20 g. HCl	5.5
Ammonia (NH_3, mol. wt. 17.032; NH_4OH, mol. wt. 35.048).	0.900	28.5	0.256 g. NH_3 0.512 g. NH_4-OH	15

The Assay of Reagents

It is essential for the assayer to be assured of the fact that his reagents are pure or at least to know to what extent they are impure and what the impurity consists of. For this reason, it is necessary to examine lots of reagents from time to time, as they come into the laboratory, by approved chemical methods, to determine their purity. Sometimes reagents or fluxes, as a result of being left exposed in the laboratory, become accidentally or purposely "salted" or contaminated with gold, silver, or base-metal values. A blank assay for metals on the reagents will readily determine this. In general, it may be stated that

the labeling of a chemical "c. p." does not necessarily make it so. Borax has been found to contain platinum.[1]

It is necessary to determine the silver in litharge and test lead, as these two reagents frequently contain some silver, due to their being usually made from lead bullion refined by the Parkes' or zinc-desilverization process, which leaves some silver in them. As litharge is almost invariably used in the crucible assay, and test lead in the scorification assay, any silver or. possibly, gold introduced into the results by their use must be subtracted, so as not to be ascribed to the ores. Most assay supply houses now furnish practically silver-free litharge and lead containing only traces of silver and no gold.

The method of determining silver and gold in litharge and test lead is as follows:

The following charge is weighed out in duplicate:

Litharge	3 a. t.
Sodium carbonate	20 g.
Silica	7 g.
Argol	2 g.
Borax glass	5 g. (as a cover)

The various ingredients are put from the scale pan on a sheet of glazed paper and thoroughly incorporated by mixing. It is essential to weigh the litharge and argol as accurately as possible with the pulp balances in use.

The incorporated charge is then transferred to a 20-g. crucible, a shallow cover of borax glass being put on top of the charge, and then fused in the muffle furnace for from 25 to 35 min. at a yellow heat (1000° C.). The fusion is considered complete when the charge is in quiet fusion, that is, when there is no more bubbling and boiling in the charge and when the only motion observable is that due to convection currents. The charge is then poured into an iron mold and allowed to solidify, which takes approximately 10 min. After this the lead button is separated from the slag by the hammer and formed into a cube. It is weighed and its weight recorded in grams and tenths of a gram in the assay notebook, a definite assay number being assigned to this assay and its duplicate. The lead button is then cupelled, the cupel being first placed in the muffle for 10 to 12 min. before the lead button is dropped into it. If the button weighs from 15 to 20 g., as it should, it will take 25 or 30 min.

[1] Rose, J. G., *Jour. Chem. Met. Mining Soc. S. Africa*, vol. IX, p. 168.

to finish the cupellation, that is, to drive off the lead. The end of this operation, in this particular instance, is denoted by the darkening of the small silver bead. The bead is then removed from the cupel after this has become cold, flattened on a small anvil with a blowpipe hammer, cleaned of adhering bone ash from the cupel by a button brush, and weighed carefully on the assay balances, the weight being recorded in milligrams and hundredths of a milligram. The weight of the bead, divided by the number of assay tons (3) taken in the assay, gives the number of ounces contained in a ton (2,000 lb.) of litharge, or the number of milligrams per assay ton of litharge.[1] If the presence of gold is suspected in the litharge, the silver bead from the cupellation, after weighing, is dropped into a parting cup filled with hot nitric acid (9 parts water: 1 part concentrated nitric acid, sp. gr. 1.42), which will dissolve the silver and leave the gold as a black residue. This residue is washed three times by decantation with cold distilled water, carefully dried, and annealed at a red heat in the muffle; after cooling, it is weighed as already described for silver. The weight of the gold is recorded and then subtracted from the weight of the original gold and silver bead. The difference in weight gives the amount of silver.

To determine the silver and gold in test lead, weigh out 3 assay tons, place in a 2.5-in. scorifier, add a pinch of borax glass, and scorify in the muffle at a yellow heat (1000° C.). As the lead oxidizes to litharge, this melts and forms a slag which, owing to the convexity of the meniscus of molten lead, falls to the side of the surface and forms the slag ring, leaving a disk of fresh lead exposed. The scorification is finished when the slag finally covers all the lead. The charge is then poured into an iron mold, the further method of procedure followed being identical with the one described for the litharge assay.

It is possible to obtain test and sheet lead with only traces of silver, and litharge practically free from silver. It is often desirable that the litharge should contain a uniform amount of silver, for whenever low-grade gold ores, deficient in silver, are assayed, silver will have to be added at some stage of the assay in order to insure parting or the complete separation of the gold from the silver. In assaying very low-grade gold ores, in which practically only gold is present, the final bead might be so small

[1] For a discussion of weights used in assaying, cupellation, and weighing, reference should be made to these subjects.

as to sink into minute cracks in the cupel and thus be lost. The addition of silver in this case, either by adding it in the metallic state or by its presence in the litharge, obviates this difficulty.

Litharge will frequently contain from 0.20 to 0.32 mg. of silver per assay ton. It is, however, not safe to assume the above figures. The test lead ordinarily bought from the supply houses contains only traces of silver.

CHAPTER IV

THE PREPARATION OF THE ASSAY SAMPLE

In this chapter, it is not the purpose to discuss in detail the theory and practice of sampling ores and metallurgic products or to describe the mechanical plant used for this purpose. The subject of sampling more properly belongs in a metallurgic treatise. The reader is referred to the important papers on this subject listed in the footnote.[1]

In most cases, the samples representing large lots are handed to the assayer so that he is usually not directly concerned as to how the samples were obtained, but, in general, he should be familiar with sampling procedure. Proper sampling is of the utmost importance, for unless the sample to be assayed accurately represents the lot of ore or metallurgic product from which it is taken, in other words, unless it is a true sample, the greatest care in the assay itself means nothing. Large amounts of money are involved in settlements made on the assay of final samples representing many tons of rich ore, matte, bullions, etc. Mills and smelters purchase ores by the carload on the assay of the final sample, and even slight errors mean loss to either the shipper or the purchaser. Where so-called *specimen* assays are made, the sampling of the small amount of pulp is usually a simple matter, although accuracy is also required.

Sampling may be classified under two heads:

1. Hand sampling:
    - *a*. Coning and quartering.
    - *b*. Alternate shovels.
    - *c*. Split shovels.
    - *d*. Riffling.
2. Machine sampling:
    - *a*. Part of the ore stream for the whole time.
    - *b*. The whole of the ore stream part of the time.

[1] Woodbridge, T. R., "Ore-sampling Conditions in the West," *Tech. Paper* 86, U. S. Bur. Mines, 1916; Keller, Edward, "The Principles and Practice of Sampling Metallic Metallurgical Materials," *Bull.* 122, U. S. Bur. Mines, 1916.

Whatever the method of sampling used, a distinct relation must exist between the weight of the sample and the size of the ore particles. Thus, if the ore particles are large (10 to 12 in. diameter), a large sample must be taken; if the particles are small (0.10 to 0.20 in.), a small sample will, if properly taken, accurately represent the lot of ore.[1] An old rule in force on Gilpin County, Colo., ores, carrying from 1 to 4 oz. gold, illustrates this:

Diameter of largest piece, inches	0.04	0.08	0.16	0.32	0.64	1.25	2.50
Minimum weight of sample, pounds	0.0625	0.50	4	32	256	2,048	16,348

The proper weight of sample for any desired size of ore particle is obtained by multiplying the known weight for the given size by the cube of the ratio of the desired size to that of the given size. This would mean that the sample always contains the same number of fragments.

As an example of mill practice by machine sampling on Cripple Creek ores of from 2 to 6 oz. gold per ton, the following is given:

The ore is crushed to pass a 1.5-in. ring, and from the total bulk a Vezin sampler cuts out one-fourth. This is passed to crushing rolls, which reduce it to 0.25-in. size. It is then elevated to another Vezin sampler, which takes out one-tenth of the bulk, the final sample being one-fortieth of the ore, or 2.5 per cent. This is then cut down and crushed finer and sampled in the usual way (alternate shovels, etc.), described farther on. In smelting works, where it is desirable to have the product going to the furnaces as coarse as possible, the above method is modified by not crushing so fine and by taking larger samples; or hand sampling is employed. The size of the sample depends not only on the size of the ore particles but also on the nature of the ore. If the values are uniformly distributed, smaller samples will do than are necessary where they are "spotted" or irregularly distributed.[2] While machine sampling, with properly constructed apparatus, is largely in use, and is most desirable when applicable, hand sampling may be accurately performed; it is

[1] Brunton, "The Theory and Practice of Ore Sampling," *Trans.* A. I. M. E., vol. XXV, p. 826; *Trans.*, A. I. M. E., vol. XL, p. 567; "Notes on Sampling," *Mining Reporter*, 7–16, inclusive, vol. XLV.

[2] Wright, L. T., "Element of Chance in the Sampling of Ores," *Mining Mag.*, vol. III, p. 353, 1910.

still widely used by smelting plants, as it avoids crushing a large part of the ore.[1]

Coning and Quartering.—The method of coning and quartering has been in use for many years and is still employed, but it is being displaced largely by the alternate-shovel method. Coning and quartering, unless carefully performed, which is difficult, is apt to be inaccurate. In this method, the thorough mixing of the ore is essential, and the mixing is supposed to be effected by coning. The cone is built up by men moving around the circumference of a circle and shoveling the ore upon the point of a cone formed by the angle of repose of the material falling vertically upon one point. The samplers—from two to eight men—move so as to follow each other at equal distances.

In order to fix the point of the cone, a rod is driven into the ground as a guide. It is evident that the shoveling must be very conscientiously done in order to have the ore distribute itself uniformly (fine and coarse) over the surface of the cone; but this uniformity is essential to the obtaining of a true sample. When the cone has been built up, it is then pulled down by the men walking around the pile and scraping the ore from the apex to the base, until a flat plaque of ore is made about 12 or 18 in. thick. Then, in the form of a cross, plates of iron are carefully centered on the pile and driven in, dividing the plaque into quarters. Two opposite quarters are removed to the bins, and the other two, representing the sample, are reshoveled into a cone and the operation repeated. The ore is then recrushed and coned and quartered again, until finally a sample of from 25 to 30 lb. is obtained. The number of recrushings depends upon the size of the first sample and the nature of the ore. The sample is then ground fine and prepared for the assay office by cutting down with a split sampler or other approved device. The whole process is slow and laborious. Three men can handle from 20 to 25 tons of sample per shift at a cost of from 45 to 50 cts. per ton.

The Alternate-shovel or Fractional Shoveling Method.—The fundamental law of sampling may be stated thus: In order properly to take a sample of ore, it is necessary to take the sample frequently, or in as many places as possible, and to take the same quantity each time at regular intervals. These conditions are

[1] For a good discussion of machine sampling, consult A. W. Warwick, "Notes on Sampling," Industrial Publishing Co., Denver, Colo.

fulfilled by the alternate-shovel method, which is conducted as follows:

The ore from the cars is dumped on a platform and men with the proper-sized and -shaped shovels put it into the bins, taking out for the sample a certain number, dependent on the nature and size of the ore pieces; *e.g.*, nine shovels are thrown into the bins and every tenth shovel is taken as a sample. If the ore is difficult to sample, sample shovels may be taken more frequently; or, if the ore is uniform, less frequently. It is usual to cut out from one-fifth to one-twentieth of the ore; but in very important or with extremely rich samples one-half or one-third may be taken. The alternate-shovel method possesses the following advantages:

1. It is more reliable and accurate than coning and quartering.
2. It is cheaper in operation.
3. It is quicker.

The quartering and the split-shovel methods are not reliable and need not be described.

At the plant of the Standard Smelting Company, at Rapid City, S. Dak., the shovel sample was passed to a Blake crusher with a 9- by 15-in. mouth opening, having an A discharge, so as to halve the crushed sample. One of the halves was fed directly to a pair of 24- by 12-in. rolls the discharge from which was again automatically halved. If a 100-ton lot was taken as a unit, the sample at this point was 2.5 tons (taking every tenth shovel), with no particle larger than 0.375 in. in diameter. The rolls discharged directly upon a plate-iron floor, where the ore was reshoveled, every fifth or tenth shovel being taken as a sample, which then amounted to 1,000 or 500 lb. This was put through a pair of 12- by 12-in. sampling rolls and crushed fine and then sampled by a large Jones split or riffle sampler, which takes halves, until, finally, a sample of between 15 and 20 lb. was arrived at. This was put through a small cone-grinding mill and, after a determination of moisture on the sample floor, was sent to the assay office. Here it was cut down to about 2 lb. by a small Jones sampler and then crushed on a buckboard to pass a 120-mesh screen, furnishing the assay sample. This sample was supposed to contain no moisture, as the latter was eliminated on the sample floor, where the percentage of moisture was determined; but as all settlements were made on dry samples, the final assay sample was again heated at 100° C. for some time

in order to expel any moisture which the sample might have absorbed in its passage from the sampling works to the assay office.[1] The assay sample was divided into four parts and put in paper sacks. One part was assayed by the seller of the ore or product; one part by the purchaser; a third part was kept for emergency; and a fourth part was laid aside for an umpire assay, if such became necessary.

The assays made by the seller of the ore and those made by the purchaser of the ore are called *control assays.* If the seller and purchaser agree within a certain limit, depending on the value of the ore, settlement is made on the purchaser's assay, or sometimes on the average of the two assays. If they do not

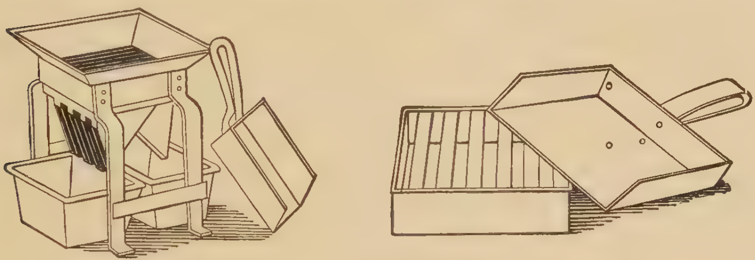

Fig. 34.—Jones riffle sampler.

agree, it is the practice for the buyer and seller to reassay their own samples or to exchange pulp samples and reassay. If they do not then agree, an umpire assayer is chosen who makes an *umpire assay*, by the results of which all parties abide, and on which settlement is made. The party that is farthest away from the result of the umpire has to pay for the assay.

Controls are made with three, and umpires with four check assays. In sampling small lots in the laboratory and cutting down for the assay sample, the principles already enumerated also apply. Riffle samplers are commonly used as well as the coning and quartering method, although this last is not recommended, even for small lots. The final pulp sample is put through a 100- or 120-mesh screen; for high-grade material, 150 or 200 mesh is better. It is then thoroughly mixed on a rubber sheet or on heavy glazed paper, spread out in a thin, broad plaque 0.25 in. thick, and small lots taken with a spatula at regular intervals, until the required weight is obtained. Figure 34 shows the Jones riffle sampler.

[1] James, G. A., "Moisture as a Source of Error in Assay Reports," *Eng. Mining Jour.*, vol. XC, p. 1047.

The form with pans is preferable to that which has half of its riffles closed.[1] The samplers should have an even number of riffles, and at least 10 or 12 of them for the best work. The sampling shovels should be of the width of the sampler and perfectly straight across the edge so that the ore will fall uniformly into the riffles and in equal quantities into each riffle. Large riffle samplers for 400- to 500-lb. samples are used in sampling works. The riffle sampler when properly used is an apparatus that will do accurate work.

Great care should be taken to clean all sampling apparatus after sampling each lot, so as to avoid "salting" samples. This laso applies to all the crushing machinery employed in the sampling.

Sampling Lead Bullion.[2]—Lead bullion is molded into bars of approximately 80 to 100 lb. weight and shipped in this form. The best method of sampling is to take dip samples at regular intervals while a lot of bars is being molded at the furnace. When the solid bars are to be sampled, about the only reasonably accurate method is to take a "saw sample." This is carried out as follows: Out of a lot of bars, every fifth or tenth bar is sawed across the middle into two pieces. The sawdust is then further cut down to the proper amount for sample and assayed.

Copper bullion is sampled in a similar manner.[3] Copper bars and slabs are often sampled by drilling. Thus a series of anodes may be systematically drilled at points laid out by means of a template or gauge, so that no two of the series are drilled at a similar place. In this way errors due to segregation of precious metal are avoided in the composite sample.

Chip or gouge samples are almost invariably inaccurate.

Procedure for Identification and Control in Commercial Assay Offices.—Professional assayers rarely mark crucibles or scorifiers

[1] Huntoon, L. D., "Accuracy of Mechanical and Riffle Ore Samplers," *Eng. Mining Jour.*, vol. XC, p. 62. The latter however, is convenient where portability is essential, as it may be made to fit compactly inside the scoop. Its capacity is small as the troughs must not be allowed to overflow. It should be used in conjunction with a large cloth, paper, or pan.

[2] Roberts, G. M., "Experiments in the Sampling of Silver Lead Bullion," *Trans.* A. I. M. E., vol. XXVIII, p. 413; Keller, Edward, "The Distribution of the Precious Metals and Impurities in Copper," *ibid.*, vol. XXVII, p. 106.

[3] Wraith, William, "Sampling Anode Copper, with Special Reference to Silver Content," *Trans.* A. I. M. E. *Bull.*, 39, p. 209, 1910; Liddell, D. M., "Sampling Copper Bars," *Eng. Mining Jour.*, vol. XC, pp. 752, 897, 953, 1095; "Saw Sampler for Copper Bars," *Eng. Mining Jour.*, vol. XC, p. 640.

but rely on keeping the individual assays in each batch in consecutive order, the origin or description of each being recorded when weighing out. Sometimes, instead of the description, a number is used which is recorded with the corresponding number elsewhere. It is, of course, equally important to identify each batch and also to take care that the batch is not reversed. The position of No. 1 in each rack or tray must be marked unmistakeably.

In case it is desired to mark certain crucibles or scorifiers unmistakeably, this may be done with a red (iron oxide) or blue (prussian blue) pencil or chalk; either gives a mark which is black while hot and red on cooling (Fe_2O_3). Another plan is to drop a little cobalt oxide into a scorifier. When copper is absent from all the samples, as in certain mining districts, a few milligrams of fine copper wire dropped into a crucible or scorifier with the charge, or added to the cupel with the lead button, will mark the cupel; 10 mg. of copper give a distinct color.

In South Africa,[1] this copper marking has been elaborated into a system. For instance, the first, fifth, ninth, etc., samples may be marked with 100 mg. of copper, the third, seventh, eleventh, etc., with half of this amount. It then becomes easy to distinguish these two sets of cupels from one another and to recognize any probable transposition of cupels or lead buttons, so as to correct the error. At some Rand mines this principle has been extended to identify the several batches of samples.[2]

The precise method of handling the samples at the various stages of work varies considerably, but, in general, it consists of working them in a series of batches, each of which goes as a unit or in a group of two or three units through the various processes of weighing and mixing with flux, fusion, pouring, button cleaning, cupellation, parting, annealing, and weighing.

For instance, in muffle melting, a muffle may hold 16 large or 24 small crucibles; accordingly, the crucible carrier, a frame of wood or sheet iron, may have 24 holes, and the corresponding number of large or small flux charges will be measured out in advance in the proper number of pots. The duplicate ore charges are then weighed out and recorded, mixed on paper with flux, poured back into their respective pots in proper sequence, covered with borax, and carried to the furnace. Number 1, the left front crucible in the rack, goes to the left rear row of muffles,

[1] Monckton, H., *Jour.* C. M. M. Soc. S. Africa, vol. VIII, p. 54, 1907.

[2] "Rand Assay Practice," p. 179 and frontispiece.

No. 24 to the front right position. When pouring, No. 24 is the first to be taken out and poured into the molds previously alined in front of the muffle. When the slags are broken, the lead buttons are placed in wooden racks and returned to them when cleaned and carried again to the cupels. The sequence of the various numbers throughout the treatment is indicated in the diagrams. The precise arrangement, left to right, and the placing of the first row front or back, varies in different offices, but the system adopted is strictly followed.

The empty crucibles, as soon as poured, are placed upside down in a large rack. If possible, this should be large enough to contain the whole day's empties. When cold, these are picked over, defective ones are thrown out, and the remainder are distributed to their respective classes. Any which have held especially rich material are usually broken to prevent their possible use on material of low grade.

```
17 0 0 0 0 0 0 0 0 24
 9 0 0 0 0 0 0 0 0 16
 1 0 0 0 0 0 0 0 0  8
```

I. Ores weighed out and set in crucible rack.

```
( 1) ( 2) ( 3) ( 4)
( 5) ( 6) ( 7) ( 8)
( 9) (10) (11) (12)
(13) (14) (15) (16)
(17) (18) (19) (20)
(21) (22) (23) (24)
       Front
```

II. Muffle fusion of 24 ores, No. 12 pots.

```
(2) (4) (6) (8) . . . (20) (22) (24)
(1) (3) (5) (7) . . . (19) (21) (23)
```

III. Pouring into double molds, beginning with No. 24.

```
 1 0 0 0 0 0 0 0 0  8
 9 0 0 0 0 0 0 0 0 16
17 0 0 0 0 0 0 0 0 24
```

IV. Tray for lead buttons from one muffle.

```
00000000 48
00000000 40
00000000 32
00000000 24
00000000 16
00000000
12345678
  Front
```

V. Cupellation of 48 buttons in small cupels.

```
1 2 3 4 5 6 7 8
0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 16
0 0 0 0 0 0 0 0 24
0 0 0 0 0 0 0 0 32
0 0 0 0 0 0 0 0 40
0 0 0 0 0 0 0 0 48
```

VI. Cupel board and parting cup trays.

CHAPTER V

WEIGHING; BALANCES AND WEIGHTS

Balances

The balance used in weighing the minute quantities of gold and silver is a delicate piece of apparatus and must be carefully adjusted and manipulated in order to give accurate results. The modern American assay or *button balance* so-called is unsurpassed for accuracy and rapidity of weighing very small masses such as the small quantities of silver and more particularly of gold obtained from ore assays represent. The most prominent makes of assay balances now on the American market are the Ainsworth, the Heusser, the Keller, the Thompson, and the Voland. In the Rand in Africa, the Oertling balance is much used. The Troemner balance is used for bullion work in the United States Mint.

The assay balance is, in every sense of the word, a precision instrument which possesses a high degree of sensitivity, sensitivity being defined as the rate of increase of the deflection of the balance beam (translated, to the pointer and scale) for a given additional load on one pan of the balance. The degree of sensitivity is indicated by the accompanying table.

Table V

Variation of weight, milligrams	Deflection of pointer over index scale, divisions	Degree of sensitivity
1/100	1	1/100
1/100	2	1/200
1/100	3	1/300
1/100	4	1/400
1/100	5	1/500

Construction.—The balance beam is made of aluminum, gold-plated brass, special silver aluminum alloys, etc., and as light as possible consistent with the requisite strength. The material

from which it is made should be non-magnetic and have a small coefficient of expansion, so that temperature changes will have but slight effect on the length of the beam. The pan hangers are frequently of a nickel-silver alloy or of german silver, and the pans of aluminium. The standards and other metal work are best made of gold-plated brass. The knife edges and the plates on which they rest are made of agate, accurately polished and ground true. The balance beam has three knife edges, which should be in line in the same plane in order to give equal sensitivity with varying loads (coplanar). The two balance arms, or the distance from the central knife edge to each of the outer knife edges, should be equal in length. This can never be absolutely attained but is very closely approximated, so that no reversed or double weighings need be made and corrections applied when a high-grade assay balance is used.

In designing balances, it is very important to preserve a mean between high sensitivity and stability, and as this latter is obtained mainly by lowering the center of gravity, which lessens sensitivity, in part by increasing friction on the knife edges, these must be constructed with extreme care and must be as nearly true as possible. Most assay balances are provided with fall-away pan rests operated by a milled head on the outside of the case. When this screw is turned to the left, the rests drop away from the pan, and on further turning the balance beam is lowered and set free so that the central knife edge rests on its bearing, and the balance is free to act.

In some balances a third set of moving supports lifts the stirrups from the end knife edges when at rest. In some, agate planes rest on the end knife edges; in others, the agates are hollowed into an obtuse V form. In some, each agate end knife-edge is replaced by two sapphire points, and there are corresponding conical holes in the agate planes.

Two principal types of balance may be distinguished. In one, including most of the older long-beam instruments, the stirrup hangers are long and the index points downward. The other, "or inverted," type has the index pointing upward, the hangers are extremely short and light, and the beam usually very short. Some portable balances omit the index proper, but one end of the beam carries a short pointer moving over a vertical scale.

It is of interest to note that the index scale should not have equal divisions of arc, but equal tangential divisions on a horizontal line.

The screw ball or *gravity bob* (see Fig. 35) is provided to adjust the center of gravity, which should be somewhat below the fulcrum knife edge A. The center of gravity is adjusted so that a weight of 0.01 mg. in the pan or on the beam will cause a deflection of from one-half to one division of the pointer. The lower the center of gravity of the balance system the more rapid the oscillation of the balance. The higher or the nearer the point of suspension the slower the oscillations and the greater

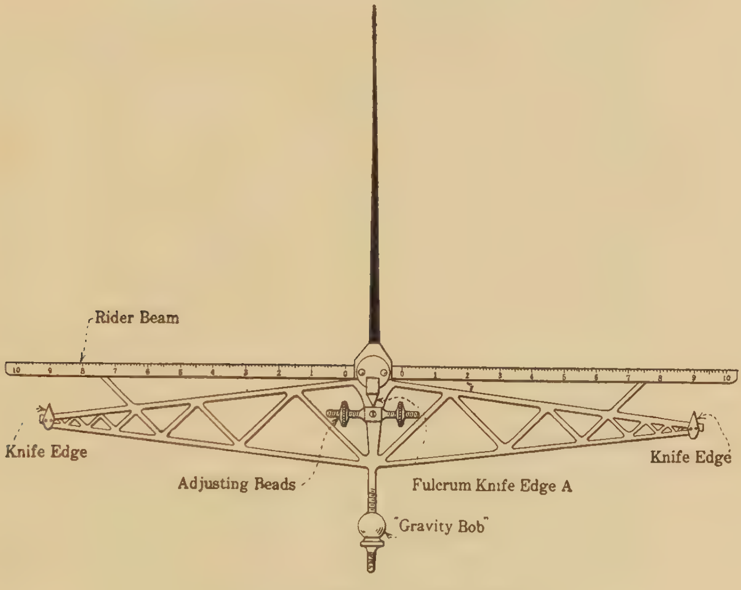

FIG. 35.—Detail of balance-beam.

the sensitivity. On either side of the center of the beam is a small milled bead on a short horizontal threaded rod, or the *adjusting beads.* These serve the purpose to adjust the balance to the *null point* or *zero point,* so that when the balance is released and settles into equilibrium the pointer will rest at the zero point of the scale. In some balances, the adjusting beads are placed at the end of the balance arms, while in others a vane or small movable horizontal lever is fixed on the beam directly above the fulcrum.

The usual rating for precision balances is the degree of sensitivity. There is another quality in precision balances which is just as important as sensitivity, namely, stability. This quality

is defined as the capacity of the oscillating system to return rapidly to the starting or zero point. The two qualities, sensitivity and stability, are opposed to each other and either one can be secured only at the expense of the other; namely, high sensitivity is associated with low stability and erratic behavior, and high stability is associated with low sensitivity or incapacity correctly to weigh small masses. The proper design of the balance, therefore, is always a compromise, and users should not be misled by claims of too great sensitivity.

A rapidly oscillating balance, if it is sufficiently sensitive, aids greatly in speed of work. Modern short-arm balances (4 to 5 in. long) are usually adjusted to a period of oscillation of 4.5 to 5 sec., giving a sensitivity of about 0.01 mg. For greater sensitivity, balances with arms 5 to 6.5 in. long and a period of oscillation 7 to 8 sec. are used. An assay balance is designed to carry only small loads, usually not more than 0.5 to 1 g. Greater loading strains the beam, leading to a change of beam length and a possible permanent "set."

The rider and rider beams are important adjuncts of the assay balance. The rider method of weighing small quantities (up to 1 mg. for assay balances) is universally used. The rider consists of a piece of platinum wire bent and shaped to fit the particular balance in use. The theory of the rider, in the limiting case of the rider beam coinciding with the balance beams on the same plane as the knife edges, is simple. Dividing the distance between the central knife edge or fulcrum and the outer knife edges into 100 parts, a rider of a given weight (1 mg.) on the division over the outer knife edge of the right beam will just balance an equivalent weight in the pan of the left beam or *vice versa*. Intervening positions of the rider give weights directly proportional to the distance from the fulcrum. Thus, a milligram rider on division 22 will balance 0.22 mg. on the pan of the opposite beam. When the rider is used on the beam in a position above that of plane of the knife edges, as is the case with most balances, the above statement still holds, as can be demonstrated.[1]

Modern assay balances are usually provided with two rider beams and riders and rider-operation mechanism for both beams.

[1] *The Theory of the Rider*, THORPE, Dictionary of Applied Chemistry, vol. I, pp. 404, 406, W. Dittmar, 1912. Consult this article for *balance* in general.

The construction is such that it is not convenient to place the zero mark on the rider beams over the central knife or fulcrum but at some small distance on each side. This arrangement then places the outer and last division on the beams beyond the outer knife edges at a distance equivalent to that of the zero mark from the center. Two riders are always used, one resting on a zero

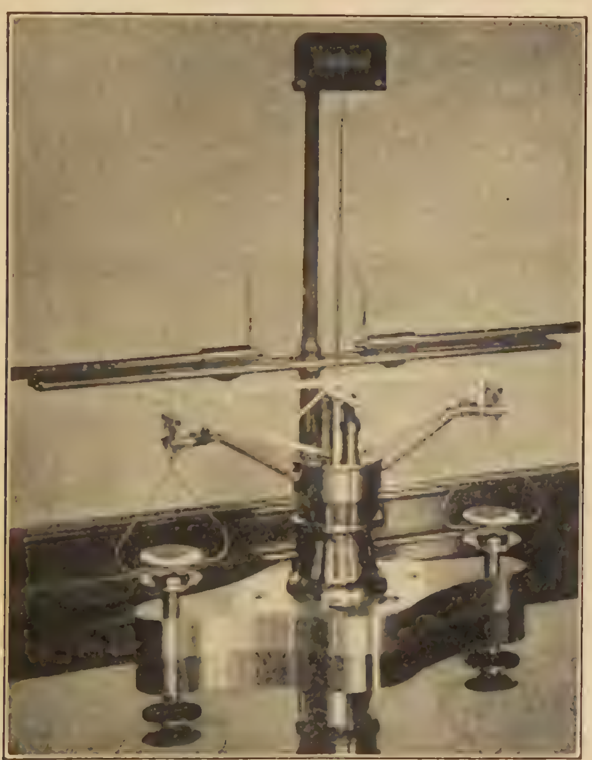

Fig. 36.—Detail of Ainsworth balance.

point, compensating for the extra distance, away from the fulcrum of the rider with which the actual weighing is done. From the foregoing discussion, it follows that the rider beam may be divided into any suitable number of divisions and the rider have other mass than 1 mg. In cases where the sensitivity of the balance, combined with proper stability, is sufficiently great, $\frac{1}{2}$-mg. riders may be used to increase the accuracy of weighing. In adjusting the balance for equilibrium, it is always necessary to have the riders in place, for if they are not, the sensitivity will

be changed, and if the riders are not equal in weight (which they should be, as nearly as possible) the adjustment is void.

Some makers provide their balances with a system of small weights mechanically operated by a lever, just as is the ordinary rider. These small weights may be in the form of riders, there being often nine weights (1, 2, 3, 5, 10, 20, 30, 50, and 100 mg.). The riders are picked up by the lever device and hung on a rack which is part of the stirrup suspension or pan hanger on the right side of the balance. In the Heusser balance, the right-hand pan hanger carries a perforated *plate* or *grid;* back of the pan hanger is a short column carrying nine movable levers. The front end of these levers has an upright cone-tipped staff which moves

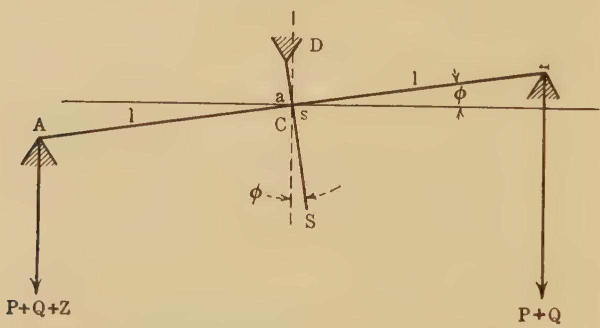

FIG. 37.—Diagram illustrating the theory of the balance.

vertically through the grid perforations. The levers are operated from the outside of the balance case by means of depressable push keys. The weights are in the form of disks, each disk having a central perforation. When in use, they are deposited in countersunk holes in the grid. They may be placed while the balance is in swing. This same balance has a mechanical pan extractor which mechanically removes the left pan from the hanger, passes it through a crystal shutter in the balance door to be loaded, and then replaces it. By means of such devices, the speed of weighing is much increased and the balance is kept closed avoiding air drafts and increasing accuracy of weighing (Fig. 42).

Balances with the refinements described are, in general, not suited to student use but of much value in commercial and works laboratories.

Simple Theory of the Balance.[1]—The following assumptions are made:

1. That the three knife edges are all horizontal and are parallel to one another.

2. That the effective lengths of the arms of the balance are equal and invariable.

In the diagram (Fig. 37), let

D denote the fulcrum knife edge.
A, B denote the terminal knife edges.
C denote the midpoint AB.
S denote the center of gravity of the beam alone.
(It is here assumed that DCS is perpendicular to AB. This is done for simplicity, since in practice the distances CD and SD are very small compared with AB.)

Let

$l = AC = CB$ = the length of each arm of the balance
$CD = a$
$SD = s$
ϕ = angle of inclination of the beam to the horizontal
G = mass of beam alone
Q = mass of each pan with suspension stirrup (supposed the same for left and right pans)
P = load in right pan
$P + z$ = load in left pan
g = the acceleration due to gravity

By taking moments of the vertical forces about the fulcrum D,

$$G \cdot s \cdot \sin\phi + (P + Q)(l\cos\phi + a\sin\phi) = (P + Q + z)(l\cos\phi - a\sin\phi)$$

$$\therefore \sin\phi[Gs + 2a(P + Q) + za] = l \cdot z \cdot \cos\phi$$

$$\therefore \tan\phi = \frac{lz}{Gs + a[2(P + Q) + z]}$$

To within the accuracy with which the sensitiveness of a balance is measured, there is no difference between $\tan\phi$ and ϕ, while z is very small compared with $(P + Q)$ and may be omitted from the denominator.

The sensitiveness of a balance is defined as the rate of increase of the deflection of the beam for a given additional load on one pan, *i.e.*, it is equal to $\partial\phi/\partial z$, or

$$\text{sensitiveness} = \frac{l}{Gs + a[2(P + Q)]}. \tag{1}$$

If GK^2 is the moment of inertia of the beam alone about the fulcrum D, K being the radius of gyration, the equation of motion of the whole moving system, when balanced, may be written

$$[2(P + Q)(a^2 + l^2) + GK^2] \times \frac{\partial^2\phi}{\partial t^2} + f\left(\frac{\partial\phi}{\partial t}\right) + g[Gs + 2a(P + Q)] \times \phi = 0,$$

where the coefficient of $\partial^2\phi/\partial t^2$ is the moment of inertia of the whole system about the fulcrum, and the expression $f(\partial\phi/\partial t)$ represents the resistance of

[1] GLAZEBROOK, Dictionary of Applied Physics, vol. III, p. 113.

the air to the motion of the beam. Hence, the period t of swing of the balance
is

$$2\pi\sqrt{\frac{2(P+Q)(a^2+l^2)+GK^2}{g\{Gs+2a(P+Q)\}}} \qquad (2)$$

that is,

$$\frac{2\pi}{\sqrt{lg}} \times \sqrt{\text{sensitiveness} \times \begin{array}{c}\text{moment of inertia}\\ \text{of the moving system}\end{array}}$$

$$\therefore \frac{t^2}{4} = \frac{\begin{array}{c}\text{sensitiveness} \times \text{moment of inertia}\\ \text{of the whole moving system}\end{array}}{\begin{array}{c}\text{length of arm of balance} \times \text{length}\\ \text{of simple pendulum which beats}\\ \text{true seconds}\end{array}} \qquad (3)$$

The performance of a balance may, therefore, be summed up as follows, with the help of equations (1) and (2):

1. If the three knife edges are coplanar under all conditions of loading of the balance, the sensitiveness is independent of the load. This condition is not fully realized in practice owing to the bending of the beam under load.

2. For a beam with three knife edges exactly coplanar so that a is zero, increased sensitiveness is obtained by reducing G and s, *i.e.:*

a. By making the beam as light as possible consistent with strength, and

b. By diminishing the distance of the center of mass of the beam from the fulcrum knife edge.

(Instability of the moving system is, of course, to be expected when the center of mass lies above the fulcrum.)

3. If the fulcrum knife edge lies just below the plane through the terminal knife edges, so that a is negative, the denominator in the expression to the right of equation (1) can be made smaller than it would be if the three knife edges were coplanar.

Hence, increased sensitiveness may be obtained in this way, but greater variation with load is found as compared with the beam which has its knife edges lying in the same plane.

The increase (or decrease) of sensitiveness with increase of load may be used as a criterion of the position of the central knife edge with respect to the plane through the terminal ones.

The question as to whether a long beam is preferable to a short one is a compromise between the following considerations:

a. For a balance designed to take a given load, an increase in the length of the beam is inevitably accompanied by an increase in its mass. Much depends on the proportionate increase of l and G.

b. For a beam of given mass, the stiffness is considerably diminished by increasing its length. Consequently, the ideal condition of obtaining coplanar knife edges for all loads is less likely to be satisfied by a long beam.

c. Even if the mass of the beam is kept constant, an increase in the length is accompanied by an increase in the moment of inertia of the moving system (*i.e.*, of beam and load) and, therefore, by an increased period of swing.

Note.—In the final choice of length of beam, other questions are involved, such as the degree of invariability of the effective length of the balance arm, and the uneven distribution of temperature along the beam.

Nearly all balances are provided with a stabilizer nut or adjustment for raising or lowering the center of gravity of the beam. For a given balance beam, increased sensitiveness is obtained only at the expense of increased period of swing. (At the same time, a good compromise may be obtained by keeping a relatively quick period of swing and reading the deflection of the beam with greater precision, say, by optical methods.)

Weights

Milligram Weights.—Weights used with the assay button balance should be of high accuracy and should be calibrated. Most balance makers furnish weights calibrated to standards set by the U. S. Bureau of Standards. The specifications for class M, or high-precision laboratory standards, call for the following: The entire weight must be of a single piece of hard, homogeneous, non-magnetic material, preferably gold or platinum plated, with fractions of a gram preferably of platinum, but aluminum may be used for weights from 20 to 1 mg., inclusive. The weights used are milligram weights, the units being as follows: 1,000, 500, 200, 100, 50, 20, 10, 5, 2, 1. Weighings below 1 mg. are made by means of the rider. The usual material for weights is platinum, platinum iridium, gold, and aluminum for units below 20 mg. Aluminum while soft gives a large size for small weights and makes for ease and accuracy in handling weights. Riders are made of platinum and should be carefully calibrated and checked, as they are quite frequently off weight.

Weights for the gold-bullion assay in which 1,000 = 500 mg. and called *millième weights* are explained in Chap. XIII.

Assay laboratories should possess a standardized set of weights against which working weights can be checked at intervals. Standard methods of calibrating weights will be found in the references cited in the footnote.[1] The U. S. Bureau of Standards will calibrate weights at comparatively small cost.

Gram Weights.—For weighing fluxes and other material, several sets of brass metric weights from 5 kg. to 1 g. are useful in the laboratory. These weights need be only of ordinary accuracy. For weighing ore pulp and other material to be

[1] Pienkowsky, A. T., "Short Tests for Sets of Laboratory Weights," U. S. Bur. Standards, *Sci. Paper* 527, 1926. Price, 10 cts.

Richards, T. W., "Methods of Standardizing Weights," *Jour.* Am. Chem. Soc. vol. 22, p. 144, 1900.

Hopkins, Zinn, and Rogers, "Standardization of Weights," *Jour.* Am. Chem. Soc. vol. 42, p. 2528, 1920.

Watson, "Calibration of Weights," "A Textbook of Practical Physics," p. 71, 1906.

assayed, both gram weights and special assay-ton weights are needed. The gram weights required range from 100 g. down to 10 mg. The assay-ton weights usually have these units: 4, 2, 1, 0.5, 0.2, 0.1, and 0.05 a.t.

The Assay-ton System.—The assay-ton system was devised by the late Prof. Charles F. Chandler, of Columbia University,

Fig. 38.—Assay ton weights.

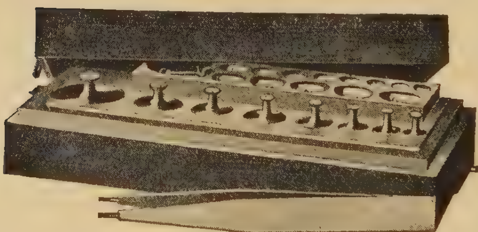

Fig. 39.—Gram weights.

and reconciles the difficulties arising from the fact that all ores, etc., are weighed by the avoirdupois system, while precious metals are weighed by the troy system. The basis of the assay ton is the number of troy ounces in 1 ton (2,000 lb.) avoirdupois.

$$\begin{aligned} &1 \text{ ton} &&= 2{,}000 \text{ lb.} \\ &1 \text{ lb. (avoirdupois)} &&= 7{,}000 \text{ troy gr.} \end{aligned}$$

therefore,

$$\begin{aligned} &1 \text{ ton} &&= 14{,}000{,}000 \text{ troy gr.} \\ &1 \text{ oz. (troy)} &&= 480 \text{ gr.} \end{aligned}$$

therefore,

$$\frac{14{,}000{,}000}{480} = 29{,}166 \text{ oz. (troy)}$$

Then, taking 1 mg. as the unit, 1 assay ton = 29,166 mg., or 29.166 g., and 1 mg. bears the same relation to 1 assay ton as 1 oz. troy bears to 1 ton of 2,000 lb. avoirdupois.

From this it follows that if 1 assay ton of ore is taken, and the silver and gold from this is weighed in milligrams, this weight will represent ounces troy per ton of ore. Figure 40 shows a set of platinum assay weights. Figures 38 and 39 show a set of assay-ton and gram weights, respectively.

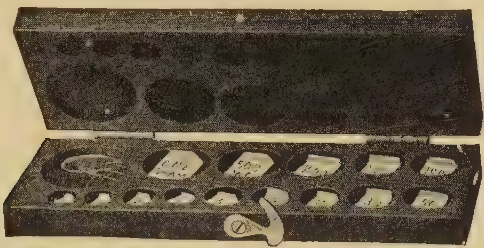

FIG. 40.—Platinum assay weights.

Practical Notes on the Assay Balance.—The balance should be set upon a firm foundation, not subject to vibration; otherwise it is apt to be frequently thrown out of adjustment. Stone or concrete piers set some distance into the ground and free from the floor are the best foundations, when the vibrations induced by moving machinery are absent. Where such vibrations occur, insulated shelf supports should be used. In those laboratories where the balance cannot be supported on stone piers, trouble may be experienced from jarring. This can largely be eliminated by supporting the leveling screws on truncated pyramids cut out of rubber packing, making the lower base of the support 2 in. square and the upper one 1 in. square, with a thickness of about 1 in. A small square of ground glass may be cemented to the top of each support to take the thrust of the leveling screw. Another method of avoiding the jar is to bore four holes ½ in. deep into the balance table top and insert No. 5 rubber stoppers on top of which a small piece of heavy sheet lead is placed, about ⅜ in. thick. For the best effect,[1] the level screws should be sunk into the lead about 3/16 in. deep. There should be two button balances provided in assay offices, one, for the weighing of silver beads, which need be of only

[1] LIDDELL, D. M., *Eng. Mining Jour.*, vol. LXXXIX, p. 305.

moderate sensitivity; and the other, for weighing gold, which should be of the best type and of high sensitivity.

One source of trouble with delicate assay balances is their tendency to become magnetized or charged with static electricity which will cause them to act in a very erratic manner during weighing. Balance beams constructed of material subject to magnetization should be avoided. When a balance of this kind

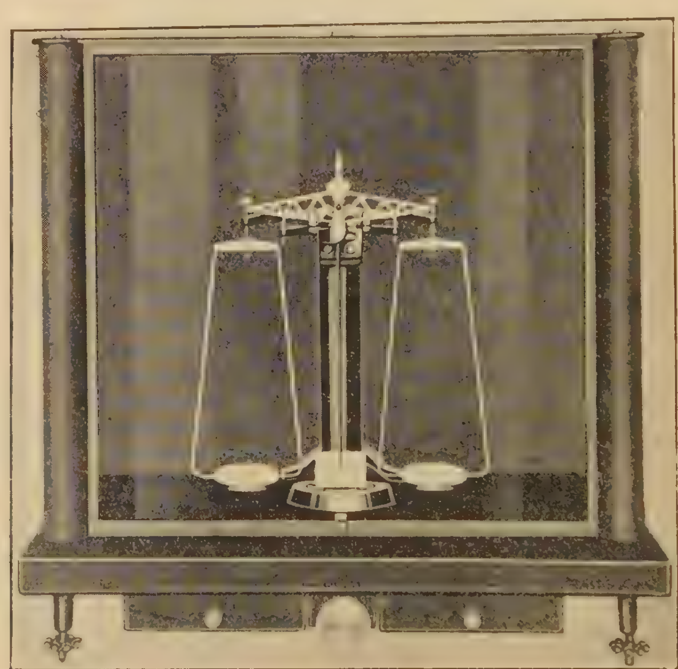

FIG. 41.—Pulp balance.

is in use, it may become necessary to change its position to avoid, in part, the magnetizing forces. For instance, the balance beam should not be parallel to a north and south line. Balances constructed of non-magnetic material may be subject to similar trouble due to charges of static electricity. This is particularly true in dry climates, either hot or extremely cold, and may be accentuated by insulating the balance from its surroundings by glass or rubber supports. When trouble of this kind occurs, it may be desirable to ground the balance by a copper wire.[1]

[1] AUSTIN A., and SWIFT HUNTER, "Balances," *Mining Sci. Press*, vol. XCVII, p. 224.

Balances which have pans that are blackened on one side and are bright on the other seem to be subject to peculiar disturbance at certain times. In this case, both sides of the pan should be blackened. The Heusser balance is made with an all-metal case which greatly aids in preventing electrical and magnetic disturbances.

It is necessary to have an even temperature in the balance room, preferably about 60° F. Sunlight should be excluded if possible, hence, the north side of the building is preferable in the northern hemisphere. The balance must not be exposed to a source of heat which will radiate unsymmetrically, otherwise unequal expansion of balance arms will cause incorrect weights. Most of the irregular and erratic behavior of balances may be traced to thermal effects. It is, hence, desirable where possible to use balances in what is essentially a dark, constant-temperature room and to use balances equipped with illuminators. In weighing, the balance door should always be closed to avoid the disturbing effect of slight air currents. The true weight of a mass can be determined only by correcting for the buoyant effect of air. The error, however, is so small that it may ordinarily be neglected.[1]

Pulp balances are shown in Fig. 41.

Weighing.—Before weighing, the balance is always thoroughly cleaned in every part from dust by a soft camel's-hair brush, made perfectly level by adjusting the leveling screws, and the pointer standardized to the null point by the adjusting beads. To do this, the balance is set in motion until the pointer swings to from 1 to 4 divisions on the scale each side of the zero mark. If the balance arms are equal in moment, the pointer will swing practically an equal number of divisions on each side, losing, however, a trifle on each swing, thus: $+4, -3.75, +3.50, -3.25, +3, -2.75$, etc., the loss being due to friction and to a gradual settling back into equilibrium. If the swings are not as outlined, the adjustment is made until they become so. The balance is then tested for sensitivity, and the adjustment made, if necessary, by moving the gravity bob. If the balance arms are suspected of being unequal in length (though this is rare in good balances), weighing by "substitution," or double weighing

[1] Ostwald, "Physico-chemical Measurements," p. 38, 1894; Ames and Bliss, "A Manual of Experiments in Physics," p. 151; Glazebrook, Dictionary of Applied Physics, vol. III, p. 117, 1923.

is adopted. In this method, the object to be weighed is placed first in one pan and weighed and then in the other, the true weight being the square root of the product of the two weights found. When the sensitivity of the balance is accurately known, no adjustment for equal moment of arms need be made, but weighing may be done by deflection after the true zero or equilibrium point is found. This is found as follows: Start the

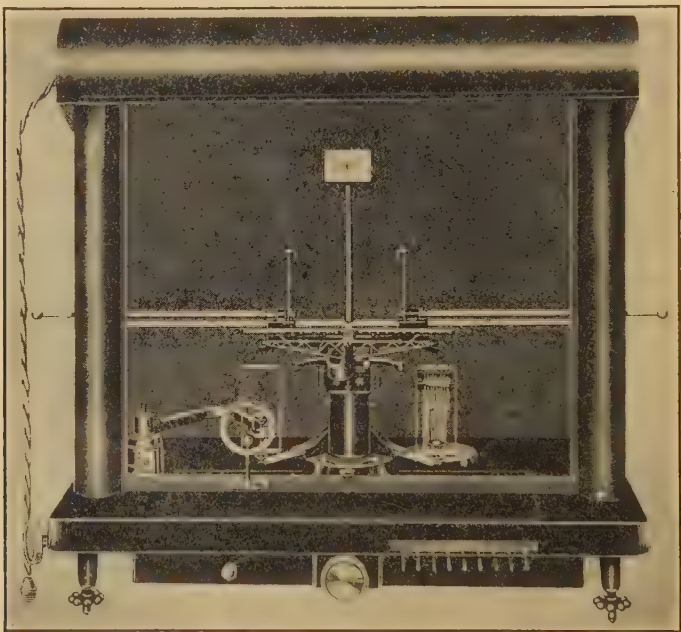

FIG. 42.—Heusser balance.

balance swinging and count swings to the left as minus and to the right as plus. Suppose the swings to be as follows: $-8, +3, -7.5$. The zero point then is

$$\frac{-8 + (-7.5)}{2} + 3 = -4.75 \text{ (divisions)}$$

$$\frac{-4.75}{2} = -2.375 \text{ (divisions)}$$

of the true zero, or true "point of rest," is 2.375 divisions to the left of the zero mark on the scale.

Then place the particle to be weighed on the right-hand pan and weigh again to determine the point of rest under these conditions. The swings are as follows: -10, $+2$, -9.5. The

sensitivity of the balance being 0.5 division deflection for each 0.01 mg., the new zero point is

$$\frac{-10 + (-9.5)}{2} + 2 = -7.75 \text{ (divisions)}$$

$$\frac{-7.75}{2} = -3.875 \text{ (divisions), new point of rest,}$$

and the weight of the particle is the difference in deflection between the two points of rest (3.875 − 2.375 = 1.5 division) divided by 0.5 or 0.03 mg. In practice, in place of two readings on one side and one on the other of the zero, it is better to make three and two readings, respectively, but the calculation becomes more complicated.

This method, however, is not generally to be recommended; the "rider" should be used for the determination of the fractional parts of the milligram. The balance should also be adjusted for equal moment of arms, as described, before weighing.

Some assayers weigh by "no deflection." They adjust the balance to the true zero, place the bead to be weighed in the right-hand pan, and then, by the addition of weights and the moving of the rider by repeated trials, balance the bead, so that, finally, when the balance is lowered gently on its knife edge, no deflection of the pointer takes place. This method, however, is not recommended, as it disregards friction and inertia and for small weights gives inaccurate results.

Weighing by substitution gives both the relative and the true weights of a substance, and the results are absolutely accurate, even when the balance is not in perfect equilibrium or the arms not of exactly equal lengths. In this method the substance to be weighed is first accurately counterpoised; it is then removed, and weights substituted for it until equilibrium is again restored. It is obvious that the weights thus substituted for the substance will represent the true weight of the substance. "In practice this method of weighing may be facilitated by using one of the larger weights, heavier than the object to be weighed, as a counterpoise, and adding weights to the object until equilibrium is established. The object is then removed, and weights substituted until the balance is again in equilibrium. The substituted weights express the real weight of the object" (Thorpe). Weighing by substitution is in use in some bullion assay offices where very great accuracy is required.[1]

[1] Smith, E. A., "The Sampling and Assay of the Precious Metals," p. 61, 1913.

In successively weighing small beads or parted gold from many assays representing one lot of ore, say ten beads from ten scorification assays representing check samples on the same lot, these are weighed separately, each weight being recorded. They may then be weighed together in one lot and the resultant weight compared as a check. The agreement should be close, else an error in weighing is indicated.

In weighing the beads or parted gold from many assays of different lots, a check may be obtained by what is termed *cumulative* weighing. In this method, the gold or bead is not removed but allowed to stay on the scale pan. The weight of the individual particle is the difference between two readings. This method has the advantage of saving time and of eliminating the constant error of the balance. It has the disadvantage that it is not possible to go back and check a suspected weighing.

CHAPTER VI

REDUCTION AND OXIDATION REACTIONS

Reduction

A reduction reaction, as particularly defined for assaying, is one in which a metal is reduced from its compounds by some reducing agent. The chemical definition is also applicable in that, in assaying, we frequently reduce a compound from a state of higher oxidation to a lower state of oxidation by means of a reducing agent.

An oxidation reaction is one in which a metal or a compound is changed to a compound of a higher state of oxidation; for example, Pb to PbO, S to SO_2, or PbO to PbO_2. Reduction and oxidation reactions frequently occur in assaying, and it is essential that the assayer be thoroughly familiar with the theory and facts. In speaking of reducing agents and reduction with special reference to assaying, we have chiefly in mind such reagents as reduce metallic lead from litharge in the crucible. The chief of these are: (1) argol, (2) charcoal or coke or coal dust, (3) flour or sugar. These are added to the charge in sufficient quantity to produce the proper size of lead button in the crucible assay. It often happens that an ore will contain reducing agents, chiefly sulphides, so that it becomes unnecessary to add an extraneous agent. In fact, it may contain an excess of reducing agent, requiring an oxidizing agent to destroy the excess.

The reduction of lead from litharge by argol is expressed by the following equation:

$$\begin{array}{c} 10PbO + \underset{376}{2KHC_4H_4O_6} = \underset{2070}{10Pb} + 5H_2O + K_2O + 8CO_2 \end{array}$$

One gram of argol will reduce 5.50 g. of lead from 5.93 or more g. of PbO. The above formula for argol is that of pure bitartrate of potassium. Argol contains as impurity a certain amount of carbonaceous matter, so that its reducing power will be increased. It will be found that the actual reducing power

of 1 g. of argol varies between 7 and 9.5 g. of lead, dependent on the argol used.

The reduction of lead by charcoal is expressed by the following reactions:

$$\begin{array}{c} 2PbO + \underset{12}{C} = \underset{414}{2Pb} + CO_2 \end{array}$$

One gram of carbon will reduce 34.5 g. of Pb. As charcoal, coal, or coke dust will contain more or less inert ash which has no reducing effect, the actual amount of lead reduced will be materially less. It will usually be found to range between 20 and 30 g. per gram of carbonaceous reducing agent used, averaging about 26 g.

Flour will reduce from 9 to 12 g. of lead per gram, depending on the nature of the flour. There is about as much difference between different samples of wheat flour as between wheat flour and corn meal, oatmeal, etc.

The common sulphides most frequently found in ores, and which give reducing powers to the ores containing them, are pyrite (FeS_2), pyrrhotite (Fe_7S_8), arsenopyrite (FeAsS), chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), stibnite (Sb_2S_3), galena (PbS), sphalerite (ZnS), and the more complex sulphides such as tetrahedrite.

The amount of lead reduced per gram of the respective sulphides varies according to the combination of conditions, which will be fully discussed.

Taking pyrite as an example, the following equation expresses the reaction which takes place when it is fused with a mixture of soda and litharge:

$$a.\quad \underset{240}{2FeS_2} + 15PbO = Fe_2O_3 + 4SO_3 + \underset{3105}{15Pb}$$

$$b.\quad 4SO_3 + 4Na_2CO_3 = 4Na_2SO_4 + 4CO_2$$

One gram of pure pyrite reduces 12.9 g. of lead. The result can readily be obtained by the following charge:

	Grams
Pyrite	3
Na_2CO_3	10
PbO	100

The result could not be obtained were the pyrite to be fused with litharge alone, as the presence of soda, a strongly alkaline base, induces the formation of sulphuric anhydride (SO_3), which

combines with soda to form sodium sulphate (Na_2SO_4). This sodium sulphate will float on top of the slag and is not decomposed by the temperature usually attained in the muffle. It separates out on cooling as a fused white mass. Its melting point is 885° C.[1] When the oxidizing action in the above charge is diminished by decreasing the litharge[2] to below 70 g., the iron is only partially oxidized to the ferric condition and the two following equations express the reactions:[3]

$$FeS_2 + 7PbO = FeO + 2SO_3 + 7Pb$$
$$2FeS_2 + 15PbO = Fe_2O_3 + 4SO_3 + 15Pb$$

The first equation will give 12 g. of Pb per gram of pyrite, and the second will give 12.9 g. The accompanying table gives the reducing powers of the various substances as determined by the litharge-soda charge given for pyrite.

TABLE VI.—REDUCING POWERS OF AGENTS

Name of reducing agent	Grams of lead reduced by 1 g. of reducing agent from a litharge-soda mixture
Argol	9.61
Flour	10.53
Sugar	11.78
Charcoal	26.0
Sulphur	18.11 (see Table VII)
Pyrite	12.24
Pyrrhotite	8.71
Stibnite	7.17
Chalcocite	4.38
Sphalerite	8.16

When no soda is present to induce the formation of alkaline sulphates, the following reaction takes place, sulphur dioxide (SO_2) being formed:

$$\underset{120}{FeS_2} + 5PbO = FeO + 2SO_2 + \underset{1036}{5Pb};$$

or 1 g. of pyrite reduces 8.6 g. of lead.

[1] WHITE, W. P., *Am. Jour. Sci.*, vol. XXVIII, p. 471.

[2] MILLER, E. H., "The Reduction of Lead from Litharge," *Trans.* A. I. M. E., vol. XXXIV, p. 395.

[3] It must be borne in mind that while we speak of a "reducing" or an "oxidizing" reaction, the reaction is really of both natures, for while litharge is "reduced," the iron pyrite is "oxidized."

In the assay, as ordinarily performed, the foregoing conditions are modified by the presence of other substances—in the main, by silica. Lead oxide readily forms silicates with silica, and the mono-, bi-, and trisilicates are easily fusible, while those of a higher degree are fusible with difficulty. When a reducing agent (argol, sulphides, etc.) is fused with a silicate of lead, or with a charge containing litharge and silica, only a little lead is reduced when the silica is present in amounts to form a trisilicate or above and only somewhat more when the silica is present in amounts to form a mono- or bisilicate. The reason for this is that the silicates of lead are not reduced by sulphides or carbonaceous reducing agents at temperatures below about 1000° C.[1] Above that temperature, reduction takes place more readily. The higher the silicate degree the more difficult is the reduction. If, however, certain other bases, such as ferrous oxide (FeO), soda (Na_2O), or lime (CaO), are present (as is the case with most ores), reduction of lead from the silicate occurs, with ferrous oxide or soda, at a comparatively low temperature; but with lime alone, only at a high temperature. The following equation expresses this condition:

$$Pb_2SiO_4 + 2FeO + C = Fe_2SiO_4 + CO_2 + 2Pb$$

No difficulty is encountered in reducing lead from the borates of lead and soda, by the ordinary reducing agents, at 1100° C. While soda influences the amount of lead reduced from litharge by the sulphides present, it has not that influence on carbonaceous reducing agents, except in so far as it may reduce the acidity of the charge and thus favor reduction.

The following charge gave results as tabulated below:[2]

	Grams
Reducing agent	1
Litharge	45
Sodium carbonate	10
Silica	7

Pyrite, in this table, shows a reduction of 9.30 g. of lead per gram, a figure to be expected when its sulphur goes off partly as SO_2 and partly as SO_3. If the soda in the preceding charge is increased, the lead button will approach the maximum reducible by pyrite.

[1] Consult *Metallurgie*, vol. IV, p. 647.

[2] Miller, Hall, and Falk, "The Reduction of Lead from Litharge," *Trans.* A. I. M. E. vol. XXXIV, p. 395.

TABLE VII.—REDUCING POWER OF AGENTS

NOTE.—Compare Table VI with this.

Name of reducing agent	Grams of lead reduced by 1 g. of reducing agent from litharge in presence of silica
Argol	9.6
Flour	10.92
Sugar	11.74
Charcoal	26.08
Pyrite	9.30
Sulphur	18.11[1]

[1] Owing to the ready distillation of sulphur, this figure is difficult to obtain; 1 g. of sulphur will usually reduce 6 or 8 g. of lead.

When carbonaceous reducing agents are used to obtain the required lead button, the nature of the charge, as regards acidity (due to SiO_2 or borax), has little influence on the size of button, provided sufficient bases, outside of PbO, are present to decompose lead silicates formed and the silicate degree does not exceed a monosilicate. The amount of litharge present has some influence. The quantity of carbonaceous reducing agent remaining constant, the size of button will increase somewhat with increasing amounts of PbO in the charge. When the reducing agent is a sulphide (frequently a natural constituent of the ore), the acidity of the charge influences, to a certain extent, the size of button obtainable. It is, however, the amount of alkaline base present (K_2O, Na_2O) that exerts the most powerful influence, its presence inducing the formation of SO_3 and, consequently, sulphates, thus reducing larger amounts of lead than when no alkaline bases are present, the sulphur going off as SO_2.

OXIDATION

Oxidation of impurities in ores is frequently necessary in order to obtain good results in the assay. When ores contain an excess of sulphides, arsenides, etc. (by an excess is meant a quantity above that which will give the required size of lead button), an oxidizing agent is required to oxidize this excess, enabling it to be volatilized or slagged. Oxidation of impurities is accomplished in one of two ways:

1. By the addition of potassium nitrate (KNO_3) to the charge (or other oxidizing agents).

2. By roasting the ore, thus using the oxygen of the air for the oxidation of impurities.

When niter is added to an assay, it reacts with the most easily oxidizable compound in the charge, which is usually the reducing agent, *i.e.*, the sulphide present. Extraneous reducing agents, such as argol, flour, or charcoal, are present simultaneously with niter only when it is desired to determine the oxidizing power of niter against these reagents. For the sake of convenience, the oxidizing power of niter is expressed in terms of lead. If finely divided lead is fused with niter, the fusion reaching a temperature of 1000° C. after ½ hour, the following reaction takes place, approximately:

$$7Pb + 6KNO_3 = 7PbO + 3K_2O + 3N_2 + 4O_2$$

or 1 g. of niter oxidizes 2.39 g. of lead. The actual number of grams of lead oxidized, determined by a considerable number of experiments, has been found to be 2.37. It must not be forgotten that the atmosphere of the muffle has a considerable influence in oxidizing or reducing the lead compounds in the contents of a crucible, especially when uncovered. The analysis of the gas caught from the fusion showed 10.75 per cent oxygen, the balance being nitrogen. Oxides of nitrogen were absent. This indicates that when niter is used in the crucible fusion, oxygen is evolved which, under certain conditions, may escape from the charge without reaction. As already stated, the niter will react with the reducing agent; expressing its oxidizing power in terms of lead is merely for convenience. In certain types of charges, *i.e.*, those containing litharge, niter, and reducing agent, or litharge, soda, niter, and reducing agent, practically theoretical results may be obtained; *e.g.*, the oxidizing power of niter as compared to charcoal is expressed by the following equation:

$$4KNO_3 + 5C = 2K_2O + 5CO_2 + 2N_2$$

or 1 g. of niter oxidizes 0.15 g. of carbon.

Taking the reducing power of pure carbon as 34.5 g. of lead, the oxidizing power of niter against carbon, expressed in terms of lead, is 0.15 × 34.5, or 5.17 g. Ten fusions of a charge composed of 85 g. PbO, 1 g. charcoal, 3 g. KNO_3, with 5 g. PbO as a cover, gave very concordant results and showed the oxidizing

power of niter to be 5.10. The reducing power of the charcoal was determined by five fusions with the same charge, omitting the KNO_3.[1] These results, of course, can also be obtained by an impure charcoal, for, taking one which has a reducing power of 26 g. of lead (this was used in the above fusions), it then contains 26.0/34.5 or 0.765 g. pure carbon per gram. If 3 g. of niter have been added to the charge, the available carbon for reduction will be 0.765 − (3 × 0.15) or 0.315 g., which will reduce 34.5 × 0.315, or 10.75, g. of lead. The oxidizing power of niter expressed in lead, then, is

$$\frac{26 - 10.75}{3}, \text{ or } 5.12 \text{ g.}$$

Considering a sulphide and niter, and it is in this connection that niter is almost invariably used, the following reaction takes place in the litharge-soda charge already mentioned:

$$6KNO_3 + 2FeS_2 = Fe_2O_3 + SO_3 + 3K_2SO_4 + 3N_2$$
$$SO_3 + Na_2CO_3 = Na_2SO_4 + CO_2$$

or 1 g. of niter oxidizes 0.39 g. of pyrite. In the litharge-soda charge, 1 g. of pyrite reduces 12.22 g. of lead; therefore, 1 g. of niter, in this instance, would oxidize 12.22 × 0.39, or 4.76 g. of lead. The accompanying table[2] shows actual results obtained for the oxidizing power of niter against different reducing agents.

TABLE VIII.—OXIDIZING POWER OF NITER

Reducing agent	Oxidizing power of niter in terms of lead, grams
Charcoal	5.15
Flour	5.09
Argol	4.76
Pyrite	4.73

It follows, therefore, that the oxidizing power of niter varies with the reducing agent used.

When the assay charge contains silica and borax glass, the above figures no longer hold, for in their presence oxygen is evolved by the niter, which escapes from the charge, as in the

[1] This finding confirms that of E. H. Miller, in *Trans.* A. I. M. E., vol. XXXIV, p. 395.

[2] *Ibid.*

case of the oxidation of metallic lead by niter. The amount of oxygen lost (thus reducing the oxidizing power of niter) is probably a function of the rate of rise of temperature, but evidence also points to the fact that silica reacts with the niter, setting free oxygen, at a temperature very close to that at which niter reacts with charcoal or at which oxygen will react with carbon. Niter fuses at 339° C. but does not give off oxygen when fused alone until 530° C. is reached. Charcoal ignites at temperatures[1] ranging from 340° to 700° C., depending upon the temperature at which it was burnt, while silica begins to react with niter at very nearly 450° C., probably according to the following reaction:

$$2KNO_3 + SiO_2 = K_2SiO_3 + 5O + N_2$$

Thus, during the period in which the temperature in the crucible gradually rises to a yellow heat (that of the muffle), oxygen escapes during the range from 400° to 500° C., etc., this last being taken as an average temperature at which charcoal will begin actively to oxidize.[2]

Niter will begin to react with argol and pyrite at practically its melting point.

The oxidizing power of niter against charcoal in charges containing silica will frequently vary between 3.7 and 4.2 g. of lead, averaging about 4 g. This is 1.1 g. lower than in the litharge-soda charge. The oxidizing power of niter against sulphides is but little lowered by the presence of silica or borax glass. When the oxidizing power of niter against pyrite (sulphides) is considered, and expressed in terms of lead, the varying reducing power of sulphides in different charges has to be taken into account. Taking as an example a charge containing considerable silica, so that a large part of the soda (alkaline base) is absorbed as a silicate, leaving but little to form sulphate from the oxidation of the pyrite, it is found that the reducing power of pyrite is 9 g. of lead, as already noted. In this charge, niter will react with pyrite as follows:

$$4FeS_2 + 10KNO_3 = 4FeO + 5K_2SO_4 + 3SO_2 + 5N_2$$

or 1 g. of niter oxidizes 0.475 g. pyrite. The oxidizing power of niter expressed in lead is then 9 × 0.475, or 4.275 g. Actually, it will be very little lower than this, as but little oxygen escapes

[1] From a number of experiments by the author, willow charcoal was found to begin reaction with niter at very close to 440° C.

[2] This is offered tentatively, as an explanation of what occurs.

without action. The actual figure obtained by experiment is very close to 4.20.

It is evident from this that the oxidizing power of niter varies with the type of charge used. It ranges, for pyrite, from about 4 g. in acid charges to 4.76 in basic charges (containing no silica). It varies still more with other sulphides. It has been the practice of assayers in making the niter fusion to run a preliminary assay in a comparatively basic charge (approximately the litharge-soda type) and use the figure obtained for the reducing power of the ore in this charge in calculating the amount of niter for the final fusion, usually made quite acid. In this way, discordant results are obtained, for both the reducing power of the ore and the oxidizing power of niter vary in the different charges.

Supposing that the preliminary assay showed the reducing power of a nearly pure pyrite to be 12 g. of lead per gram of ore. Using a 0.5 assay ton in the final fusion, on this basis the amount of lead reduced would be 12×15, or 180 g. Subtracting the weight of the lead button, 20, from this leaves the equivalent of 160 g. of lead to be oxidized. Taking 4 as the oxidizing power of niter in the final charge, 40 g. of niter would be added. But in the final charge, owing to its acidity, the reducing power of the pyrite is but 10 g. of lead per 1 g. of ore, and the total reducing power of 0.5 assay ton is 150 g. It, therefore, follows that the final result will show no button. The oxidizing power for niter which should have been used is $\frac{12}{9} \times 4$, or 5.3, and 31 g. of niter added. This, then, would give approximately the proper-sized button. As the range of reducing power for pyrite is from about 9 to 12.2 g. of lead, according to whether the charge is acid and contains little soda or is of the litharge-soda type, the most satisfactory way to determine the amount of niter to add is to have the nature of the preliminary charge the same as that of the final charge and then use the figure 4 to 4.2 as the oxidizing power of niter.[1] The following charges are recommended to determine oxidizing and reducing powers:

Preliminary Assay No. 1	Preliminary Assay No. 2
5 g. pyritous ore	5 g. pyritous ore
8 g. SiO_2	8 g. SiO_2
100 g. PbO	100 g. PbO
12 g. Na_2CO_3	12 g. Na_2CO_3
Borax glass cover	3 g. KNO_3
	Borax glass cover

[1] This has reference to pure dry KNO_3. Pure dry $NaNO_3$ has an oxidizing power of about 4.75 to 5.0.

The difference in weight of the lead buttons of preliminary assays Nos. 1 and 2, divided by 3, will give the oxidizing power of niter in the type of charge used. The weight of the button of preliminary assay No. 1, divided by 5, gives the reducing power of the ore.

Preliminary Assay No. 3

5 g. pyritous ore
12 g. Na_2CO_3
100 g. PbO
Salt cover

It will be noted that the reducing power of the ore is greater with No. 3 than that obtained in preliminary assay No. 1. In order to determine the reducing power of argol and charcoal, make up the following charges in duplicate:

Preliminary Assay No. 4

5 g. SiO_2
60 g. PbO
10 g. Na_2CO_3
2 g. argol
Borax glass cover

Preliminary Assay No. 5

5 g. SiO_2
60 g. PbO
10 g. Na_2CO_3
1 g. charcoal or coke or coal dust
Borax glass cover

In order to determine the oxidizing power of niter as compared with charcoal, make up the following charge in duplicate:

Preliminary Assay No. 6

5 g. SiO_2
60 g. PbO
10 g. Na_2CO_3
1 g. charcoal, etc.
3 g. KNO_3
Borax glass cover

Calculate results as directed for niter in pyritous ores.

Certain basic ores will have an appreciable oxidizing power, so that when the usual amount of reducing agent is added to the charge to obtain a 20-g. lead button, it is found that, due to the oxidizing power of the ore, the button is deficient in size. The oxidizing ingredients of an ore are generally hematite (Fe_2O_3), magnetite (Fe_3O_4), and manganese oxides, *e.g.*, MnO_2. The reaction which takes place is as follows:

$$2Fe_2O_3 + C = 4FeO + CO_2$$

One gram of Fe_2O_3 requires 0.037 g. of carbon to reduce it to FeO.

In order to determine the oxidizing power of an ore, make up the following charge, if the ore consists mostly of base; when considerable silica is present in the ore, decrease the silica in the charge correspondingly:

1 a. t. of ore
20 g. Na_2CO_3
90 g. PbO
15 g. SiO_2
1.5 g. coal
Borax glass cover

CHAPTER VII

THE CRUCIBLE ASSAY; ASSAY SLAGS

In almost every instance, when a crucible assay is to be made, the ore and the fluxes added are thoroughly incorporated by mixing, so that, theoretically, at least, every particle of the ore is in contact with a particle or particles of fluxes and reducing agent, the most favorable condition to produce a thorough reaction among them. The separation of the precious metals is dependent upon their affinity for metallic lead, forming an alloy of lead, gold, and silver, in which lead greatly preponderates and which readily settles by gravity from the balance of the ore and fluxes which have united to form a slag. The ore to be assayed, in all instances, must be in a finely crushed condition, varying, in American practice, from 80- up to 200-mesh material. What takes place within the crucible depends upon some or all of the following factors:

1. The fineness of crushing. Are all the particles of gold and silver or their alloy present entirely set free from the inclosing gangue? In some ores, this takes place with much coarser crushing than in others. In other ores, the metals are so finely disseminated that all are not set free within the limits of crushing as carried out.

2. The mode of occurrence of the gold and silver. Is it in the free state, as is most generally the case with gold, or are the precious metals in the form of a more or less complex mineral compound (tellurides, argentite, etc.), which must be decomposed before the gold and silver will alloy with the lead?

3. The physical properties of the slag produced, *e.g.*, its formation point, its fluidity at temperatures somewhat above its formation point, and its fluidity after superheating.

4. The chemical nature of the slag, its acidity or basicity, the nature of the bases present, more particularly copper, zinc, antimony, manganese, iron, etc.

If a crucible be broken open and its contents examined shortly after fusion has commenced, these will be found to consist of a

heterogeneous mass through which are scattered innumerable particles of lead, both microscopic and macroscopic. The larger particles have been formed by the coalescence of the smaller particles gradually settling through the charge toward the bottom of the crucible to form the final lead button as the temperature rises and the charge becomes more fluid and less resistant. It is evident that the completeness of the collection of the precious metals depends upon the main factors already outlined. The temperature at which carbon begins to react with PbO to form Pb[1] is 530° to 555° C., well below 884° C., the melting point of PbO. The formation point of a borate silicate, PbO, Na_2O, $4SiO_2$, $2B_2O_3$ (Seger cone 0.022), the constituents of which are contained in nearly all assay charges, is 590° C.

In the fusion of a mixture containing silica, various bases, and borax glass, the silicate-borate having the lowest formation point will form and then, as the temperature rises, absorb either silica or base or both, as these are in excess of the ratio required to form the lowest formation-point compound. If the temperature does not rise high enough to cause this absorption, the excess of silica or base or both will remain in suspension in the formed silicate borate, practically, in an unaltered condition. If the formed silicate, etc., constitutes the greater part of the mass, there will be an imperfect non-homogeneous slag; if the excess of silica or base forms the greater part of the material, there will be a slightly fritted mass.

Taking the simplest case, and also the most uncommon, that of an ore containing free gold completely liberated by crushing, the particle of lead,[2] formed at a comparatively low temperature, can unite at once, as soon as formed, with the gold particle not inclosed in gangue and commence settling to the bottom to form the lead button. It is evident that, in this instance, the homogeneous fusion and chemical decomposition of the ore are immaterial. Taking, however, the far more common case, in which the metals are not completely liberated by crushing, it is evident that the particle of gold still inclosed within the gangue cannot be reached by the lead already reduced, and it becomes

[1] Doeltz und Graumann, *Metallurgie*, vol. IV, p. 420. According to Roscoe and Schorlemmer, *Treatise on Chemistry*, vol. II, p. 865 (1907), CO reacts with PbO to form Pb, at 100° C. H reacts with PbO to form Pb at 310° C.; Mostowitsch, *Metallurgie*, vol. IV, p. 648.

[2] There will be probably be many particles of lead for each gold particle present, so that no gold will escape for lack of lead.

practically essential to hold the lead in place until the ore particle containing the gold is thoroughly broken up chemically and liquefied, so that the lead can absorb the gold. If the lead settles through the charge before this decomposition takes place, gold will remain in the slag. The only way to control this condition is

a. By fine crushing, liberating the metals as completely as possible.

b. By the choice of a slag having the proper physical properties, *i.e.*, a low formation point and a viscous nature near the formation point but perfectly fluid at a somewhat higher temperature.

c. By a comparatively slow fusion during the early stages of the assay, to prevent, as much as possible, the rapid settling away of the lead particles through the still existing interstices of the charge.

Where compounds of the precious metals are in the ore, such as argentite (Ag_2S), tellurides, calaverite, and sylvanite, ($AuAgTe_4$), etc., these are readily decomposed by the litharge as follows:

$$Ag_2S + 2PbO = 2PbAg + SO_2$$

The tellurides will be especially considered in Chap. XI, on Special Methods of Assay.

Assay Slags

An assay slag from the crucible assay consists, in most instances, of silicates and borates of metallic bases. While usually of a homogeneous nature, a slag is rarely a chemical compound. It is to be considered, in most cases, as a complex "solid solution," this term as applied here including both the crystalline isomorphous mixtures, or "mixed crystals," and the amorphous glasses. As an example: Litharge with silica forms certain silicates which are chemical compounds, but which have not been definitely determined, though very likely Pb_2SiO_4 is one of them, judging by cooling curves which have been taken.[1] This silicate is capable of dissolving either PbO or SiO_2 and forming homogeneous solid solution within certain limits, the solid solutions in cases when the silica contents are above 11.94 per cent—corresponding to Pb_2SiO_4—being glasses.

[1] W. Mostowitsch, *Metallurgie*, vol. IV, p. 651; Hilpert, S., *Metallurgie*, vol. V, p. 535.

In a similar way, all the common bases, Na_2O, K_2O, FeO, CaO, MgO, Al_2O_3, ZnO, and MnO form silicates which are soluble in each other when molten and which when frozen will form either complex isomorphous mixtures or amorphous glassy solid solutions. An assay slag is, therefore, usually a complex "solid solution." Boric acid and alkaline borates act similarly to silica, and if borax is used in the fusion the final slag will be a complex "solid solution" of silicates and borates of PbO, Na_2O, FeO, CaO, etc., dependent upon the bases in the ore and the fluxes used.

Silicates are defined in degree by the ratio of oxygen in the base to that in the acid. The chemical classification is as follows:

Table IX.—Silicate Degrees (Mineralogical)

Name	Oxygen ratio, base to acid	Example
Orthosilicate....	1:1	$MgO.FeO.SiO_2$
Metasilicate.....	1:2	$MgO.CaO.2SiO_2$
Sesquisilicate....	1:3	$K_2O.Al_2O_3.6SiO_2$
Bisilicate........	1:4	$CaO.2SiO_2$

The metallurgical classification is made on the same basis, *i.e.*, oxygen in the base to that in the acid, but is somewhat different. It is the one adopted in this book.

Table X.—Silicate Degrees (Metallurgical)

Name	Formula, RO (base)	Formula, R_2O_3 (base)	d
Subsilicate........	$4RO.SiO_2$	$4R_2O_3.3SiO_2$	0,5
Monosilicate......	$2RO.SiO_2$	$2R_2O_3.3SiO_2$	1,
Sesquisilicate......	$4RO.3SiO_2$	$4R_2O_3.9SiO_2$	1,5
Bisilicate..........	$RO.SiO_2$	$R_2O_3.3SiO_2$	2
Trisilicate.........	$2RO.3SiO_2$	$2R_2O_3.9SiO_2$	[illegible]

Borates may be classified in a somewhat similar manner.

In general, it may be stated that the higher the silicate degree the more infusible is the mixture and that a polybasic mixture, one of many bases, is more easily fusible than one of few. These general statements are not without exceptions, for certain bisilicates and trisilicates have a lower fusing point than the corre-

sponding monosilicate, etc. What the fusibility of the silicates will be also depends greatly upon the base. PbO, Na_2O, and K_2O give easily fusible silicates; FeO and MnO give comparatively readily fusible silicates; Al_2O_3, CaO, and MgO difficultly fusible silicates. When, however, silicates of all these various bases are mixed and go into solution as a homogeneous mass, the effect of this mixture on the melting point of the mass is often to lower it. In fact, the silicate mixtures are to be looked upon from the same point of view as metallic alloys; there may be eutectic mixtures, *i.e.*, mixtures of two or more constituents

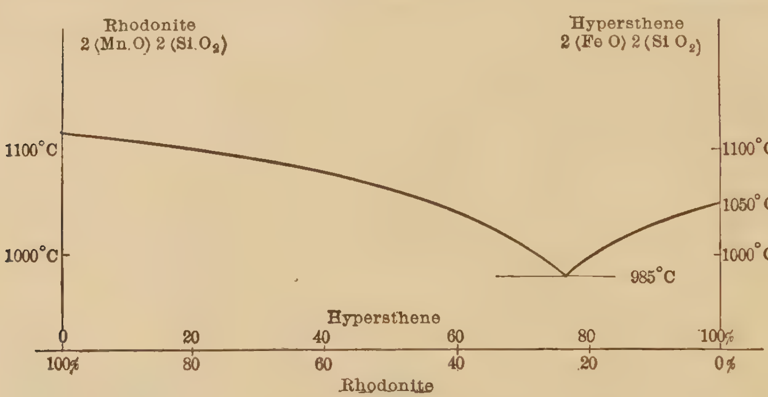

FIG. 43.—Freezing-point curve; rhodonite-hypersthene.

which have a lower melting point than either of the constituents, as is illustrated in Fig. 43.[1] In the footnotes are cited a number of systems that have a particular bearing on assay slags.[2]

The eutectic mixture, or the composition of lowest melting point in the series, occurs at 20 per cent hypersthene (the bisilicate of iron) and 80 per cent rhodonite (the bisilicate of manganese). The melting point of this mixture is 985° C., which is considerably lower than that of either constituent alone. In the series $CaSiO_3 - Na_2SiO_3$, a minimum occurs in the freezing-point curve at a composition of 80 per cent Na_2SiO_3 and 20 per cent $CaSiO_3$, the freezing temperature being 920° C.

[1] VOGT, J. H. L., *Die Silikatschmelzlösungen*, vol. II, Oslo.

[2] HILPERT, "$PbO - PbSiO_3$," *Metallurgie*, vol. VIII, p. 157, 1911.

VAN KLOOSTER, "$NaBO_2 - Na_2SiO_3$," *Zeit. Anorg. Chem.* vol. 69, pp., 122–131, 1911.

MOSTOWITCH, "Decomposition of $PbSO_4$ by SiO_2," *Trans.*, A. I. M. E. vol. 55, p. 744, 1916.

while the freezing point of Na_2SiO_3 is about 1010° C. and that of $CaSiO_3$ is 1505° C.[1]

Typical Assay Slags.—A slag of low formation temperature and considerable viscosity at that temperature corresponds to Seger cone 0.022 – $Na_2O.PbO.4SiO_2.2B_2O_3$, 590° C. This may be written $PbO.4SiO_2.Na_2B_4O_7$.

By calculation from the atomic weights, the following charge will yield this slag:

	Grams
PbO	33.6
SiO_2	36.1
$Na_2B_4O_7$	30.3

Another slag, corresponding to Seger cone 0.017 and melting at 740° C., may be desirable for aluminous ores:

($Na_2O.PbO.Al_2O_3.6SiO_2.2B_2O_3$), which may be written ($Na_2B_4O_7.PbO.Al_2O_3.6SiO_2$).

The following charge will yield this slag:

	Grams		Grams
$Na_2B_4O_7$	22.7	Al_2O_3	11.5
PbO	25.2	SiO_2	40.6

TABLE XI.—ASSAY SLAGS[1]

Formula	Silicate degree	Approximate temperature (centigrade) at which fluid	Remarks
1. $2Na_2O.SiO_2$	Monosilicate	1070	Vitreous, colorless, transparent.
2. $Na_2O.SiO_2$	Bisilicate	1090	Stony, white, crystalline.
3. $2PbO.SiO_2$	Monosilicate	1030	Vitreous, light yellow, transparent.
4. $PbO.SiO_2$	Bisilicate	1050	Vitreous, light yellow, transparent.
5. $Na_2O.FeO.SiO_2$	Monosilicate	1070	Very fluid, stony black.
6. $Na_2O.FeO.2SiO_2$	Bisilicate	1070	Vitreous, black.
7. $PbO.FeO.SiO_2$	Monosilicate	1100	Resinous, black.
8. $Na_2O.PbO.SiO_2$	Monosilicate	1020	Vitreous, yellow green.
9. $Na_2O.PbO.2SiO_2$	Bisilicate	1030	Vitreous, yellow green.
10. $2(PbO.FeO.CaO)3SiO_2$	Monosilicate	1110	Vitreous, black.
11. $Na_2O.PbO.FeO.CaO.2SiO_2$	Monosilicate	1030	Vitreous, black, contains square crystals.
12. $Na_2O.PbO.FeO.CaO.4SiO_2$	Bisilicate	1100	Vitreous, black.
13. $2(Na_2O.PbO.CaO)3SiO_2$	Monosilicate	1090	Stony, light yellow.
14. $2(Na_2O.FeO.CaO)3SiO_2$	Monosilicate	1150	Viscous, stony, gray brown
15. $2(Na_2O.PbO.FeO)3SiO_2$	Monosilicate	1030	Vitreous, black.

[1] WEST, ELMER E., Laboratory, S. Dak. School Mines, 1904.
Stony slags indicate incomplete solution of some of the ingredients.

[1] WALLACE, R. C., *Zeit. Anorg. Chem.*, vol. LXIII, p. 2.

A partial replacement of the silica by borax glass in the foregoing slags will appreciably lower the formation points.

Bases such as FeO, CaO, MgO, MnO, BaO, and Al_2O_3 are present in greater or lesser quantity in almost all ores, and SiO_2 is present in practically every ore, so that such slags as those outlined must necessarily be made. The easily fusible bases PbO and Na_2O serve to lower the formation point of the slag. If it is accepted that the composition of the slag in the assay is practically the constant factor, it is evident that when the approximate composition of the ore is known, either basic or acid fluxes will be added in such proportions as to produce the proper slag decided upon. The most desirable constitution for an assay slag, in general, is that of a monosilicate or a sesquisilicate; sometimes, but more rarely, a bisilicate. If the ore is basic, a bisilicate may be approached; if acid, a monosilicate or even a subsilicate, in order to insure complete decomposition of the ore.

The accompanying table will simplify slag calculations. It may be added that the degree of accuracy attainable by the use of a slide rule is ample for all work of this class:

TABLE XII.—THE CALCULATION OF SLAGS[1]

Unit Molecular Base Ratio; e.g., PbO: Na_2O: FeO, etc. = 1:1:1

One part of base by weight	Parts of other bases necessary						Parts of SiO_2 necessary for monosilicate
	Na_2O	PbO	CaO	Al_2O_3	FeO	ZnO	
Na_2O	1.000	3.590	0.903	1.646	1.160	1.311	0.486
PbO	0.279	1.000	0.252	0.459	0.323	0.365	0.136
FeO	0.862	3.095	0.779	1.419	1.000	1.130	0.419
CaO	1.108	3.976	1.000	1.823	1.284	1.452	0.539
Al_2O_3	0.608	2.181	0.549	1.000	0.705	0.797	0.886
CuO	0.780	2.801	0.704	1.284	0.905	1.023	0.379
ZnO	0.763	2.738	0.689	1.255	0.885	1.000	0.371

One part by weight of SiO_2 requires to form the monosilicate	Na_2O, 2.07 parts	PbO, 7.36 parts	CaO, 1.86 parts	Al_2O_3, 1.14 parts	FeO, 2.40 parts	ZnO, 2.70 parts	CuO, 2.63 parts

[1] Based on Balling's table.

When a bisilicate is to be calculated, the silica required for a monosilicate is determined and then multiplied by two. *Vice*

versa: When the bases for the monosilicate have been calculated and a bisilicate is to be formed, the bases must be divided by two. The same reasoning applies to other silicate degrees.

Example of the Calculation of an Assay Slag.—The problem is to calculate a charge to produce the following monosilicate: $Na_2O.PbO.FeO.CaO.2SiO_2$. Taking as the unit 10 g. of Na_2O, it follows from the preceding table that the weights of the substances required are

		Grams
Na_2O	10×1	= 10.0
PbO	10×3.59	= 35.9
FeO	10×1.16	= 11.6
CaO	10×0.903	= 9.03

The silica required will be:

		Grams
for the Na_2O	10×0.486	= 4.86
PbO	35.90×0.136	= 4.86
FeO	11.60×0.419	= 4.86
CaO	9.03×0.539	= 4.86
Total		19.44 SiO_2

The silica might equally well have been determined by calculating it for one base and multiplying that figure by the number of oxygen molecules in the bases present, after having reduced the slag formula to its lowest possible terms.

Before making up the charge, it is essential to remember that the Na_2O, in this instance, is furnished in the form of Na_2CO_3, which contains approximately 58 per cent of Na_2O, and that the FeO is furnished by hematite ore of the following approximate composition:

Fe_2O_3, 80 per cent; SiO_2, 17 per cent; and that 100 parts of Fe_2O_3 yield 90 of FeO.

The lime is furnished by limestone, $CaCO_3$, practically pure.

It is also necessary to provide a lead button; so extra litharge must be furnished. To reduce the lead, coal dust is added. Some of the coal will be used up to reduce the Fe_2O_3 to FeO. Hence, the following calculations are to be made: 10 g. Na_2O are required; therefore $^{10}/_{58} \times 100 = 17.2$ g. of Na_2CO_3 must be added. PbO contains 92 per cent of Pb; therefore, in order to obtain a 20-g. lead button, $\frac{20 \times 100}{92} = 22$ g. of PbO must be added, in addition to the 35.9 g. for the silicate—a total of

57.9 g. of PbO. Eleven and six-tenths grams of FeO are required. Fe_2O_3 consists of 90 per cent FeO and 10 per cent O_2; and as the ore is 80 per cent Fe_2O_3, $\frac{11.6 \times 100}{0.90 \times 80} = 16.1$ g. of ore will be required. The limestone contains 54 per cent CaO; therefore, $\frac{9.03 \times 100}{54} = 16.7$ g. of limestone will be required.

The coal in use has a reducing power of 20 g. of lead per gram of coal.

The following reaction takes place between carbon and the Fe_2O_3:

$$2Fe_2O_3 + C = 4FeO + CO_2$$

One gram of Fe_2O_3 requires $^{12}\!/_{320} = 0.037$ g. of charcoal. But as the coal used is only $\frac{20 \times 100}{34.4} = 58$ per cent as strong as carbon, the following quantity will have to be added to the 16.1 g. of Fe_2O_3 to reduce it:

$$\frac{0.037 \times 16.1 \times 80}{0.58} = 0.82 \text{ g. coal}$$

To this must be added 1 g. for the reduction of the 20-g. lead button, giving 1.82 g. of coal to be added.

Since the iron ore contains silica, this is to be deducted from the silica calculated. The amount of SiO_2 in the ore is 16.1 $\times$ 17 per cent $= 2.74$ g.

The correct charge then is

Grams		Grams	
17.2	Na_2CO_3	16.7	Limestone
57.9	PbO	16.7	Silica (19.44–2.74)
16.1	Fe_2O_3 (iron ore)	1.82	Coal
	Salt cover		

Following is the calculation of the same slag but for a quartz ore containing 95 per cent SiO_2. The formula for the slag is $Na_2O.PbO.FeO.CaO.2SiO_2$. Taking as the unit 1 assay ton of ore, or, in round numbers, 30 g., this will contain 28.50 g. of SiO_2. These 28.5 g. are to be divided into four equal parts to satisfy the four bases present. Therefore, 7.1 g. of SiO_2 will go to such an amount of each base as will form a monosilicate.

7.1 g. SiO_2 require $7.1 \times 2.07 = 14.7$ g. Na_2O
7.1 g. SiO_2 require $7.1 \times 7.36 = 52.25$ g. PbO
7.1 g. SiO_2 require $7.1 \times 2.40 = 17.04$ g. FeO
7.1 g. SiO_2 require $7.1 \times 1.86 = 13.20$ g. CaO

The Na_2CO_3 required is $\frac{14.70 \times 100}{58} = 25.4$ g.

The PbO required is $52.25 + 22 = 74.25$ g., including the lead button.

The $FeCO_3$ (siderite) required is $\frac{17.04 \times 100}{62} = 27$ g.

The limestone required is $\frac{13.20 \times 100}{54} = 24.4$ g.

The complete charge is

1 assay ton ore		27 g.	$FeCO_3$
25.4 g.	Na_2CO_3	24.5 g.	$CaCO_3$
74 g.	PbO	1 g.	Coal
	Salt cover		

In one case, the ore is of a basic nature—hematite and limestone (17 g. of each)—and in the other case, it is of an acid nature—quartz—yet the slag produced is the same in both cases. This brings out the fact that the slag is the constant and that fluxes are added of such nature and in such quantity, determined by the ore, as to produce a slag of fairly constant composition. It is to be noted that the slag made in the two assays contains four bases, PbO, Na_2O, FeO, CaO, and that these are present in unit molecular base ratio. As a matter of fact, the assayer rarely adds CaO or FeO as fluxes, but when these are present in the slag, they are derived from the ore. The bases added as fluxes are practically limited to three, PbO, Na_2O, and, at times, K_2O, so that when an ore consisting chiefly of SiO_2 is to be assayed, the slag made will approximate a monosilicate and borate of lead oxide and soda, the soda coming from soda ash and borax, the potash from niter or potassium carbonate.

The table of assay slags given mentions only those in which the bases are present in the unit molecular ratio. It is evident that where an ore is considered in which numerous bases are present, these are not contained in the unit molecular ratio, so that the formula of the slag made will rather have this general form:

$$(xPbO, yNa_2O, zFeO, tMgO)vSiO_2,$$

in which, for a monosilicate, considering the letters as oxygen coefficients, $x + y + z + t = 2v$. In order to get a slag of low formation point, the coefficients of the more infusible bases, such as CaO, MgO, Al_2O_3, will have to be materially smaller than those of the more fusible bases, PbO, Na_2O, and FeO.

In assay practice, it is neither possible nor desirable to make analyses of ore before assaying for gold and silver. The assayer, however, is supposed to have a good working knowledge of lithology and mineralogy, which will enable him to form a correct judgment of the contents of his ore within fair limits. It will be comparatively easy for him to tell at once whether he has limestone or dolomite or an ore containing much limonite or hematite or the iron sulphides; or whether magnesia, baryta, or other bases are present and in what general proportions. Following are analyses of siliceous and lead-antimonial ores:

TABLE XIII.—SILICEOUS ORES

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Gold, ounces per ton	0.63	0.85	3.35	2.00	0.78	0.90
Silver, ounces per ton	2.00	6.08	1.75	0.62	1.00	
Silica, per cent	65.38	80.00	80.90	84.80	77.38	93.72
Iron, per cent	13.40	7.50	9.94	7.50	3.54	2.67
Sulphur, per cent	11.40	4.40	4.53	0.75	4.42	0.69
Arsenic, per cent	0.90	2.00	0.29	0.00	0.55	0.02
Antimony, per cent	Trace	Trace	Trace	Trace	Trace	0.089
Tellurium, per cent	0.003	Trace	0.007	Trace		
Zinc, per cent						
Copper, per cent	0.02	0.004	0.013	0.008	Trace	
Manganese, per cent	Trace	0.54	Trace	0.96	......	0.082
Alumina, per cent	5.43	1.79	1.70	1.02	2.80	3.53
Lime, per cent	2.10	1.70	0.50	0.90	0.56	
Magnesia, per cent	0.20	......	Trace	......	Trace	

TABLE XIV.—LEAD-ANTIMONIAL ORES

	No. 1, per cent	No. 2, per cent	No. 3, per cent
Silica	60.1	57.65	59.50
Ferrous oxide	5.2	0.70	4.60
Alumina	9.5	1.40	9.00
Magnesia	2.68	2.09	3.00
Lime	Trace	Trace	Trace
Lead	10.6	16.86	10.1
Antimony	4.4	11.84	7.55
Sulphur	0.5	......	0.44
Water	0.3	.....	0.40

TABLE XV.—ANALYSES OF HEMATITE AND LIMESTONE

Hematite		Limestone	
	Per cent		Per cent
Silica	14.20	Silica	1.94
Ferrous oxide	73.68	Alumina and ferric oxide	0.68
Alumina	5.03	Magnesia	0.18
Lime	0.57	Lime	53.61
Manganous oxide	0.19	Carbonic acid	43.81
Phosphorus	0.101	Water	0.11

These analyses are given to show what the chief base constituents may be and how ores will range from acid to basic types. Whenever sulphides are present, it is to be noted that the oxidation of these leaves basic oxides to be fluxed.

At times, instead of silicate and borate slags, it is desirable to make oxide slags in the crucible assay. This, of course, can be done only when silica is absent from the ores or when a very large excess of litharge is used in the fusion. Litharge, which melts at 884° C., possesses the property of dissolving or holding in suspension certain quantities of other metallic oxides. These slags are discussed in the chapter on the Assay of Impure Ores.

The charge for the monosilicate of lead and soda is (using the unit molecular base ratio):

TABLE XVI.—CHARGE FOR LEAD-SODA SLAGS

	Monosilicate	Bisilicate
Silica or quartz ore, assay ton	0.5	0.5
Sodium carbonate, grams	26	13
Litharge, grams	55	28
Borax glass	Cover	Cover

Allowing for a 20-g. lead button, the charges will be:

	Monosilicate	Sesquisilicate	Bisilicate
Quartz ore, assay ton	0.5	0.5	0.5
Sodium carbonate, grams	26	20	13
Litharge, grams	77	63	50
Charcoal, grams	1	1	1
Borax glass	Cover	Cover	Cover

All of the above charges will yield satisfactory slags in an ore assay if the ore is of the nature described. The cheapest in point of cost is No. 3; No. 2 is the one most frequently made.

Color of Slags.—Most slags from ore assays will be from light to very dark green in color or almost black, this color being due to various proportions of ferrous silicate. When iron is absent, the color of lead silicates (yellow) may predominate or white and gray or colorless slags, due to silicates of CaO,MgO, ZnO, etc., may be produced. Copper produces red slags, due to cuprous silicate which may be streaked with green. Manganese, when but little iron is present, gives purplish slags. Cobalt gives blue slags. When much lime is present in an ore, this is best calculated to a bisilicate or even higher, while the other bases can be calculated to the monosilicate.

Size of Lead Button.—The size of the lead button requires some consideration. The use of lead to collect gold or silver is an instance of the partition of a solute (precious metal) between two immiscible solvents (slag and lead), comparable with the partition of iodine between water and carbon tetrachloride; the proportion left in the slag depending on the relative solubilities in the two solvents and on their relative quantities. Doubling the weight of the lead button should approximately halve the amount of gold left in the slag, but a too large button is inconvenient. A fairly satisfactory rule is to aim at a button weighing about 15 g. plus half the weight of ore in the charge; thus 0.5 a.t. of ore would indicate a 22-g. button, 2 a.t. about 44 g. A corresponding amount of litharge then must be added to the constituents of the flux adapted to the ore charge.

CHAPTER VIII

CUPELLATION

Cupellation has for its object the oxidation of the lead in the gold, silver, etc., alloy to PbO, which, in part (98.5 per cent), is absorbed by the cupel and, in part (1.5 per cent), volatilized. The silver and gold of the alloy are left as a metallic bead. The cupels in which the process is carried out are shallow porous dishes, made generally of bone ash, or magnesia, produced by calcining magnesite. Portland cement may be used as a cupel material.

Leached wood ashes (particularly from beech wood) and lime and magnesia have also been used for cupels. A mixture of bone ash and leached wood ashes, in the proportion of 1:2 and 2:1, respectively, has been used and is said to give a much smaller absorption of the precious metals than bone-ash cupels.[1]

Bone-ash Cupels.—Bone ash consists mainly of tricalcium phosphate, $Ca_3(PO_4)_2$, with a little calcium fluoride and magnesia and several per cent calcium oxide or carbonate. Many analyses are scattered through the literature but are difficult to compare, as they are stated in different ways and must often be calculated from analyses of the original bone. There is less difference among the ash obtained from the bones of such different sources as man, the ox, and the tortoise (84 to 88 per cent calcium phosphate) than among different analyses from the ox, as stated by different authorities; considerable variations are due to differences in age and feeding.[2] The more thoroughly organic matter has been extracted from the bones by boiling before burning the more free is the ash from sulphate and chloride, which occur in the associated organic matter.

Analyses 1 and 2[3] (Table XVII) are calculated from the analyses of bones; column 4 gives the range of a number of other

[1] KERL, *Probir Kunst*, p. 91, 1886.

[2] BROOKMAN, "Berichte," p. 388 (1892); ZELESKY, "Hoppe-Seyler's Untersuchungen," see THORPE, "Dictionary of Applied Chemistry," vol. I, article Bone Ash; TROWBRIDGE and WOODMAN, *Jour. Ind. Eng. Chem.*, vol. I, p. 725, October, 1909.

[3] HEMTZ, Erdmann's *Jour. prakt. Chem.*, vol. XLVIII, p. 24, 1839.

analyses published, in which all the phosphorus is calculated as calcium phosphate. When well burned, there is often but little carbonate, as indicated by the small loss on ignition, but unless washed thoroughly the calcium oxide remaining may injure the hands of operators making cupels, unless they are protected by gloves or by greasing. A. J. Firth[1] gives analyses of impure South African bone ash containing much carbonate and recommends leaching with very dilute hydrochloric acid, washing, and again calcining; W. Bettel[2] suggests extracting with 2 per cent ammonium chloride. In any case, the burnt bones should be washed after crushing to separate the fine material from the coarse portion and also to free the ash from soluble material and unburned carbon. A most objectionable impurity is sand or siliceous grit, which may be derived from the millstones sometimes used in grinding the ash or from imperfect preparation of the bones or from carelessness in burning. This may occur up to 6 per cent or more, in which case the bone ash should be rejected for cupels.

A high percentage of loss on ignition, after drying at 130° C., and over 1 per cent of material insoluble in hydrochloric acid (usually silica) are evidences of carbonate and of extraneous matter. The presence of $CaCO_3$ is very undesirable in bone ash for cupels, as it begins to give off CO_2 at 800° C., about the temperature of the beginning of cupellation, causing a serious spitting of the lead button, which entails a loss of the precious metals. Cupels should not be kept where the nitrous fumes from parting can be absorbed by them, as these will form $Ca(NO_3)_2$ with any CaO that may be present, which also is decomposed about the temperature of cupellation. Bone ash melts at about 1450° C. (Hempel).

The physical nature of the cupel, especially as regards porosity, is very important. For this reason, there should be a careful adjustment of the relative amounts of different-sized particles present. Practically, only the fraction of 1 per cent of the bone ash should remain on a 30-mesh screen. If there is an insufficiency of fine particles in the bone ash, the cupel will be too porous and cause a relatively heavy absorption of gold and silver. If the bone ash is too fine, the cupels made from it will

[1] Chem. Met. Soc. S. Africa, *Proc.*, vol. IV, p. 684; *Jour.* vol. IV, p. 176, October, 1903.

[2] *Proc. Chem. Met. Soc.* S. Africa, vol. II, p. 599.

be too dense, prolonging the cupellation and causing losses, mainly by increased volatilization.

The following is a screen analysis of the bone ash commonly purchased but rather coarse:

		Per cent
Through a	20-mesh screen	100
On a	30-mesh screen	2.90
On a	40-mesh screen	6.40
On a	60-mesh screen	10.04
On a	80-mesh screen	2.00
On a	100-mesh screen	11.20
Through a	100-mesh screen	68.88

Cupels should be as uniform as possible as regards density and for this reason are best made by machine, in which a constant pressure may be obtained, rather than by hand molds.

TABLE XVII.—ANALYSES OF BONE ASH

	Ash of sheep bones	Ash of cattle bones	Bone ash from various sources	Apatite
$Ca_3(PO_4)_2$	84.39	83.07	80 to 92	92.26
CaF_2	4.05	3.88	0.5 to 4	7.74
$CaCO_3$	9.42	10.0		
$Mg_3(PO_4)_2$	2.15	2.98		
CaO	.....	.....	5 to 8	
MgO	.....	.....	1 to 3	

For making cupels on a moderately large scale, the Iler machine (Fig. 44), operated by a foot lever, is one of the best, as it is simple and does not readily get out of order, while the motions are easily carried out. The bone ash is swept into a cylinder in which a plunger rises and compresses it against a heavy iron plate; on swinging the plate aside, a similar motion expels the finished cupel. Several patterns of this machine have been introduced. It might be improved by substituting a somewhat longer wrought foot lever with a larger pedal, as the cast-iron ones supplied with the machine sometimes break after long use. The machine is made with interchangeable sleeves for cupels of different diameters, and the height of the cupel is determined by the amount of bone ash fed. In using

this machine, and most others, it is advisable to wipe the working faces from time to time with an oily cloth and always to leave a pad in the cylinder when the machine is left idle. When worn, the plunger can be slightly turned down and repolished and a smaller sleeve fitted to it.

For obtaining exactly equal pressures in making cupels with a machine of this type, an extended lever with a box into which a fixed weight of lead shot is allowed to run can be used. Air pressure may be employed.

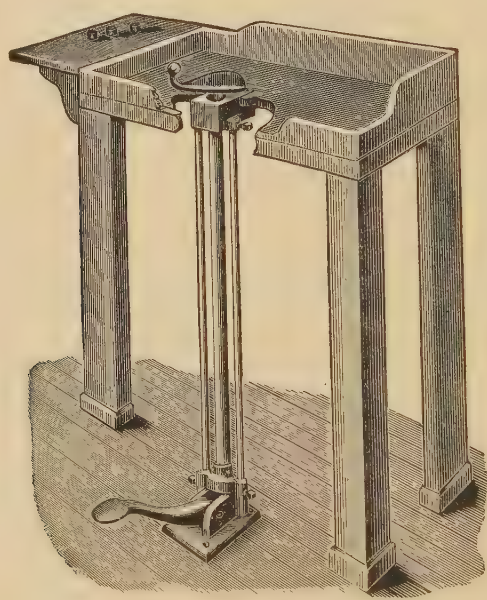

FIG. 44.—Cupel machine.

In some manufactured cupels, a high polish or glaze is given to the face by rotating the plunger under pressure; this prevents the formation of "beads" on the surface of the cupel but does not appear to affect absorption into the body of the cupel.

The rim of a cupel should have a narrow but definite ring, about 1/32 in. wide, sloping slightly toward the cavity. If the rim is made with a "feather edge" to give the cavity its maximum diameter, it is easily broken. Manufactured cupels are often made conical, that is, somewhat smaller at the base; this form is more easily ejected from the mold.

The rate at which cupels can be made depends much on the operator. One man was timed who never made over 6 or 8 per minute; another made 18 per minute for considerable periods; another made up to 27 per minute for short spurts. All of these were using a machine of the Iler type. Some other machines are more rapid. Figure 45 illustrates a hand cupel mold.

With a hand mold and mallet, 200 cupels per hour is a fair rate.

Before using cupels for assays, they should be dried for at least 3 weeks to a month and then should be tested for absorption of precious metals by cupelling a weighed quantity, (200 mg.) of c. p. silver with 20 g. of lead at the proper temperature, 850° C., and the loss noted. It should not exceed from 1.5 to 1.8 per cent.

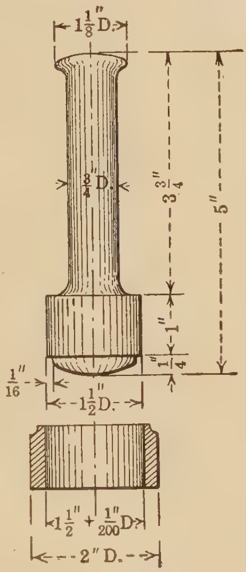

FIG. 45.—Hand cupel mold.

The bone ash to be made into cupels is mixed with from 8 to 12 per cent of water, just sufficient to make it collect into balls when squeezed in the hands. Some assayers dissolve a little potassium carbonate (pearl ash) in the water or mix with it a little molasses. Such additions are quite unnecessary, and the presence of organic matter is detrimental to the cupels. After making, the cupels should be carefully and slowly dried. If possible, cupels should be several months old before using. In the Royal British Mint no cupels less than 2 years old are used for bullion assays.

If cupels are too rapidly dried, or have been made up too wet, they crack and check when placed in the furnace and make the assays conducted in them unreliable.

The importance of good cupels cannot be overestimated. Very frequently, inaccuracies in the assays are due chiefly to the cupel. The shape of the cupel has some influence on the loss of precious metals by absorption. If the cupel cavity is very flat and shallow, so that the molten lead covers a large area and has little depth, the time of cupellation is decreased as the surface exposed to oxidation is increased; but as the absorption of precious

metals is probably a function of the area exposed, it will be larger in shallow cupels.[1]

Magnesia Cupels.—Of recent years, the so-called *patent* cupels have come into wide use, especially in England and South Africa and, to a lesser extent, in the United States. These cupels are made almost invariably of a magnesia base. This magnesia is produced by calcining crude Austrian, Californian, or Turkish magnesite and is used largely in the steel industry for basic refractory brick.

The composition is about 90 per cent MgO and 10 per cent impurities, chiefly CaO, Fe_2O_3, Al_2O_3, and SiO_2. The cupels are invariably very hard and firm, of a brown color, and are formed under high pressure. The exact composition of the cupels is generally a trade secret. Magnesia cupels cannot very readily be made in the laboratory, as can bone-ash cupels, and in almost all instances their cost is higher. A number of brands are on the market, as the Morganite cupel, made by the Morgan Crucible Co., Battersea Works, London, those made by Deleuil, Paris, and the Mabor, Scalite, Velterite, Star, etc., brands. Morganite cupels, 31.5 mm. top diameter (about 1.25 in.) the common size, cost $3.80 per 100 in St. Louis.

The chief virtue of the patent cupel appears to be that in some places they are cheaper and that they are less fragile than those made of bone ash. They are much used in South Africa except for the bullion assay.

The properties of various types of cupels are discussed in a section to follow.

TABLE XVIII.—ANALYSES OF PATENT OR MAGNESIA CUPELS AND CUPEL MATERIALS

	I	II	III	IV	V	VI
Ignition loss	0.77	0.4	0.75	14.40		Under 5
Insoluble (silica and clayey matter)	15.02	16.9	14.25	14.05		3 to 6
Alumina Iron oxide	2.33		1.95	 5.8	8.18 0.31	 1
Magnesia	72.3	70.8	79.25	64.5	91.62	85
Lime	9.33	5.6	4.05	1.25		3 to 4

I, II, III, satisfactory cupels sold in the U. S.; IV, unsatisfactory; V, Mabor, used in S. Africa (A. T., FIRTH, Chem. Met. Soc. S. Africa, *Proc.*, vol. IV, p. 684; *Jour.*, vol. IV, p. 176, October, 1903); VI, typical California calcined magnesite.

[1] EDMANDS, H. K., *Eng. Mining Jour.*, vol. LXXX, p. 245.

Portland-cement Cupels.—Satisfactory cupels may be made of ordinary portland cement, provided the amount of mixing water is carefully adjusted.[1] The amount of water should be 8 per cent of the weight of the cement. If less than 5 per cent water is used, the cupels are too fragile; if 20 per cent is used, they will not readily pass the cupel machine. Upon heating, cupels with less than 5 and with more than 15 per cent water cracked about the edges. Cupels made of one-half cement and one-half bone ash give good results.

Cement cupels are very cheap as compared with bone ash. Cement will cost from 35 cts. to $1 per 100 lb., while bone ash costs from $5 to $8 per 100 lb. Cement cupels should be thoroughly dried before use, otherwise they will develop cracks during heating.

TABLE XIX.—ANALYSES OF PORTLAND CEMENTS MADE OR USED IN THE UNITED STATES

Average of Nearly 100 Analyses of Many Different Brands

	Minimum	Maximum	Average
Silica	20.2	23.6	22.0
Alumina	5.0	8.9	7.1
Ferric oxide	2.2	4.8	3.2
Lime	58.9	65.0	62.5
Magnesia	0.3	3.4	2.3
Sulphur trioxide	0.4	2.3	1.5
Specific gravity	3.07	3.20	3.12

PROCESS OF CUPELLATION[2]

When ready to cupel lead buttons, the cupels are placed, empty, in the red-hot muffle and allowed to remain there for at least 10 min. in order to expel any moisture or organic matter present (if molasses water has been used in making them up). If the buttons were placed into the cold cupel, the lead would melt before the expulsion of all of the remaining moisture, which would then pass up violently through the molten lead,

[1] HOLT, T. P., and N. C. CHRISTENSEN, "Experiments with Portland Cement Cupels," *Eng. Mining Jour.*, vol. XC, p. 560; MERRITT, J. W., "Cement *vs.* Bone-ash Cupels," *Mining Sci. Press*, vol. C, p. 649.

[2] The description which follows refers, in the main, to bone-ash cupels.

causing what is termed *spitting, i.e.*, the projection of small lead particles, carrying gold and silver from the cupel. Some cupels, made from bone ash containing $CaCO_3$, will commence to spit after the cupellation has proceeded for some time and the temperature has risen to above 800° C. This can be stopped by pulling the cupel to the cooler (front) part of the muffle, although the cupellation, after spitting, is to be considered unreliable. When a piece of wood or coal is placed in the muffle to "open up" lead buttons, the cupels absorb gases at times, which, later on, when the temperature rises, are again expelled, with a spitting of the lead.

When the lead button is put into the hot cupel, the lead melts (326° C.) and is covered by a gray-black scum. If the lead button is practically pure, as it should be, this black scum disappears when the lead reaches a temperature of 850° C. This is called the "opening up" or "uncovering" of the lead button. The molten lead then appears bright, begins to "drive or show motion on the surface," and active and rapid oxidation commences. Lead buttons should uncover as soon as possible in the muffle. If other and more difficultly fusible metals, such as Cu, Fe, etc., are present, the temperature of uncovering and that required for cupellation are higher. These foreign metals should, however, as a general rule, be absent.

Little flakes of PbO form on the surface of the molten lead and slide down the convex surface of the button and are absorbed by the porous mass of the cupel. The process of cupellation is dependent upon the relation of the surface of the cupel to that of the molten lead alloy and the litharge which is formed by oxidation. There is a great difference between the surface tension of molten lead and litharge, and while litharge can "wet" the bone-ash surface and, hence, be absorbed, molten lead cannot do so, or only to a very slight extent, and, hence, is not absorbed. In the same manner, metallic silver and gold, left on the cupel by the oxidation of the lead, will not be absorbed by the cupel. As will be noted farther on, during cupellation, there is always a loss of precious metal the greater part of which is lost by absorption by the cupel. Whether this absorption is due to some small part of the lead alloy's passing into the cupel or to an oxidation of some silver with consequent absorption has never been definitely determined. It is true that the different cupel materials and the physical condition of the cupel as regards

porosity influence absorption; the greatest factor, however, is temperature of cupellation, a comparatively slight increase of temperature causing a marked increase in absorption. Whether this increased absorption is due to an increased oxidation of the precious metal or a decrease in the surface tension of the lead alloy is open to question.

The temperature of cupellation is by far the most important single factor in the operation. Three distinct temperatures must be considered: (1) the temperature of the cupelling lead; (2) the temperature of the muffle, by which is meant the temperature of the interior of a blank cupel, directly adjoining the one containing the lead; and (3) the temperature of the air in the muffle, near the cupel. The vital temperature is that of the cupelling lead, but as this is difficult to measure except by special apparatus, the "muffle temperature," which always bears a distinct relation to the temperature of the cupelling lead, is used hereafter in designating the *temperature of cupellation.*

The temperature of cupellation for pure lead buttons should be 850° C. to "uncover" the button; this may be lowered to about 770° C. during the major part of the cupellation but must be raised again to about 830° C. near the end to finish the operation. This applies to bone-ash cupels. The temperature of the lead itself during cupellation is higher than that indicated by the blank cupel near it, owing to the rapid oxidation of the lead. This is shown by the brighter color of the lead.

Any foreign metals, as Cu, Sb, Fe, Zn, etc., which are present are oxidized (some by the PbO formed) and absorbed by the cupel, if not present in too large amounts.

$$Cu + PbO = Pb + CuO$$

Such elements as Sb, As, and Zn, when present in the button, are, in part, volatilized as oxides and, in part, absorbed. When cupellation for silver is carried on, the temperature should not be above 820° C., in which case crystals of litharge (feathers) form on the side of the cupel toward the muffle mouth. If the temperature is too low for the cupel to absorb practically all of the PbO successfully, these feathers form low down in the cupel. When the temperature is about right, they form near the upper rim of the cupel. It is, however, to be noted that the draft through the muffle influences the formation of feather litharge; *i.e.*, if the draft is strong, feathers will form, although

the temperature is somewhat above 820° C. During cupellation, the door of the muffle should never be left wide open but should be set slightly ajar, so that the cold air will not strike directly upon the cupels. When silver and gold are cupelled for, owing to the higher melting point of the silver-gold alloy, the finishing temperature will have to be 860° C. at least.

As the cupellation proceeds, the percentage of lead in the alloy decreases and that of Ag and Au increases. The litharge thrown off from the center of the button is in larger specks and brilliant, and the button assumes a more rounded form. When this phenomenon appears, the cupel should be pushed back into the hotter part of the furnace or the temperature of the furnace raised somewhat. When the last of the Pb goes off, large buttons are covered with a brilliant film of colors (interference colors), and the button appears to revolve axially. The colors then disappear, the bead becomes dull and then again takes on a silvery tinge.

If now the temperature of the muffle is below that of the melting point of silver (962° C.) or below that of the gold-silver alloy constituting the bead, or if the cupel be withdrawn from the furnace, the "blick" or "brightening" or "flash" of the bead takes place; *i.e.*, the bead suddenly becomes very bright, at the moment of solidification, owing to the release of the latent heat of fusion, which raises the temperature of the bead very much for a short time. The bead has been in a state of surfusion, *i.e.*, in a state of fusion below its true freezing point, toward the last of the cupelling operation; and if it be lightly jarred or the temperature allowed to drop still lower (by taking it out of the muffle), it suddenly congeals and assumes a state normal (solid) to the temperature existing. The release of the latent heat, raising the temperature of the bead, causes the "brightening." The brightening of very small beads is rarely noticeable. Silver and gold beads still containing small amounts of Pb or Cu do not brighten so noticeably. If even minute quantities of rhodium, iridium, ruthenium, osmium, or osmium iridium are present, buttons will not flash. Platinum and palladium are excepted.

Silver beads after cupellation, and at the moment of solidification, also "sprout." According to Gay-Lussac, molten silver dissolves twenty-two times its volume of oxygen, measured at the freezing point. Later researches[1] have proved this practically correct. At 1020° C., molten silver will hold 19.5 volumes of

[1] Donnan and Shaw, *Jour. Soc. Chem. Ind.*, vol. XXIX, p. 987; Sieverts and Hagenacker, *Zeit. Phys. Chem.*, vol. LXVIII, p. 115.

oxygen (at 760 mm. and 0° C.), and at the melting point somewhat more. For any given temperature, the oxygen dissolved is proportional to the square root of the oxygen pressure. In air at 760 mm. pressure, the oxygen has a partial pressure of 150 mm., and the volume of oxygen dissolved by molten silver under assay conditions is 9.65 volumes at the freezing point of silver. The oxygen is dissolved either as monatomic oxygen or as silver oxide (Ag_2O), in dilute solution. It is probable that this silver oxide, not being soluble in solid silver, is dissociated with explosive violence, with the liberation of oxygen, when the silver solidifies.

This oxygen, suddenly expelled when the bead solidifies, causes a cauliflower-like growth on the bead or sometimes a simple rupture. Small particles of silver may even be projected from it and cause a serious loss. When gold is present in the silver bead to the extent of 33 per cent or more, sprouting does not take place. Silver beads containing small quantities of Pb, Cu, Zn, Bi, etc., will not sprout, so that if a button does sprout it is a sign of purity.

Buttons below 5 mg. in weight do not sprout readily; large buttons, however, do. Sprouting can be prevented by slow cooling in the muffle or by having ready a hot cupel which can be set, inverted, over the one holding the bead and withdrawing both from the muffle, thus cooling the bead slowly. Sprouted beads are to be rejected as an assay.

When cupelling for silver alone, or for silver and gold, it is necessary to watch the end of the cupellation carefully and to remove the cupel promptly about 30 sec. to 1 min. after the bead has become dull. A heavy loss of silver commences if the silver buttons are kept beyond that time in the furnace. If silver is not to be determined, but gold only, the buttons may be left in for 5 to 10 min. without loss of gold. Gold beads will retain minute amounts of lead which cannot be removed by permitting the bead to stay in the muffle.

It is to be noted, however, that silver-lead alloys containing between 80 and 90 per cent of silver also show the phenomenon of sprouting or developing a cauliflower-like growth on solidification.[1]

[1] Friedrich, K., *Metallurgie*, vol. III, p. 398.

A similar growth may occur with gold-lead or gold-silver-lead alloys under similar conditions, the lead being largely converted into oxide which includes minute sphericles of an alloy poorer in lead. A similar superficial growth occurs when bullion bars containing a little lead are exposed to air while red hot.

The bead, when cold, is taken from the cupel with a pair of pliers and cleaned of bone ash by flattening somewhat with a hammer. It should be examined with a glass to make sure that no bone ash adheres to it.

The bead should be either white or yellow, depending on the amount of gold present, round and not flat (the latter indicating the presence of foreign metals), and should possess a crystalline surface where it adhered to the bone ash. It should be firmly attached to the bone ash of the cupel; if it is not, this fact indicates that lead is still present. It should also have no rootlets extending into the cupel. The cupel, after cupellation, should

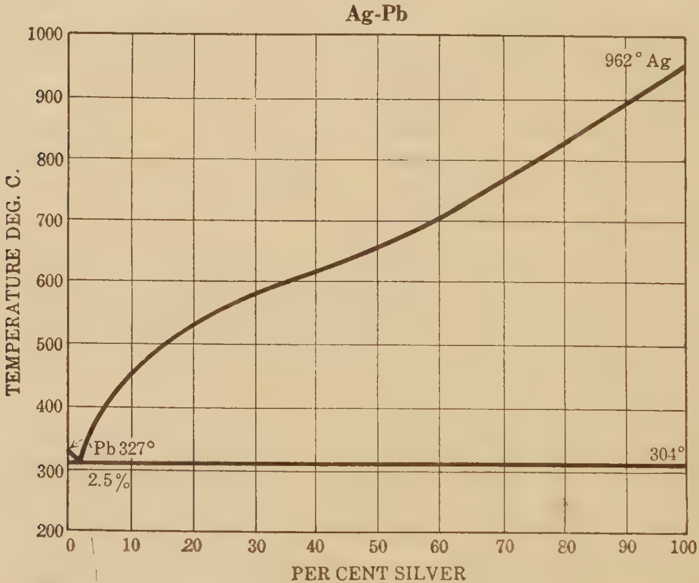

FIG. 46.—Freezing-point curve. Silver-lead.

be smooth and firm, not fissured and cracked, and of a light-yellow color when cold. Other colors indicate the presence of foreign metals.

The freezing-point curve of lead-silver (Fig. 46) will give some idea of the proper temperature of cupellation. A lead button is to be considered as an alloy of lead and silver (or gold) which in the process of cupellation undergoes the change from practically pure lead to that of pure silver (or gold).

A 20-g. button containing 200 mg. of silver contains 1 per cent of Ag. An alloy of lead and silver containing 2.5 per

cent of Ag is of "eutectic composition" and melts at 304° C., the melting point of pure lead being 327° C. Most assay buttons will contain very much less than 1 per cent of silver and will melt practically at the melting point of lead. Leaving out of consideration for the moment that lead "uncovers" at 850° C. in an oxidizing atmosphere and the proper temperature required to cause a ready absorption of PbO by the cupel, it is evident that for a lead button weighing 20 g. and containing 20 mg. of silver (0.1 per cent), the temperature required to keep the button molten ranges from 327° to 304° C., until the button has decreased thirty-nine-fortieths in weight by the loss of Pb, practically the entire time of cupellation.

When the button has reached one-fortieth of its original weight, the temperature required to keep it molten will rapidly increase, according to the curve, as more lead is oxidized, until, in order to prevent freezing and get pure silver, a temperature of 910° C. and slightly above must finally be reached.[1] In order, however, to cause a rapid formation of PbO and its ready absorption by the cupel and not have heavy losses of Au and Ag, it is found that a temperature of about 850° C. is best for the main part of the cupellation. It is evident, however, that in order to finish the cupellation, the heat must be raised toward the end, otherwise the alloy of lead and silver, as it increases in silver percentage, will tend to freeze, *i.e.*, to solidify. It is also to be noted, however, that this tendency, with most lead buttons of ordinary silver contents, is not reached until very near the end of the cupellation. It is an old saying amongst assayers that "a cool drive and a hot blick" are essential to a good cupellation. In the cupellation for silver, it would seem, at first sight, that a final temperature of 962° C. were necessary in order to prevent freezing and to obtain a silver bead free from lead. The phenomenon, however, of the "surfusion" of the silver, *i.e.* silver remaining in a molten state below its true melting point, due, probably, to its formation from its lead alloy by the oxidation of the lead, appears to indicate that this temperature is not necessary. It is true, nevertheless, that the finishing temperature, depending somewhat upon the amount of silver present, ought not to fall much below 910° C.

It is plain that buttons may be cupelled at temperatures much above those stated, but the loss of silver and gold, both by

[1] While the melting point of silver is 962° C., this temperature is not necessary, as surfusion takes place.

absorption and by volatilization, is very much increased with the higher temperatures.

The reasoning outlined for silver applies also to gold, except that, owing to the somewhat higher melting point of gold (1063° C.), the finishing temperature should be a little higher. The freezing-point curve for gold-lead is shown in Fig. 47.[1]

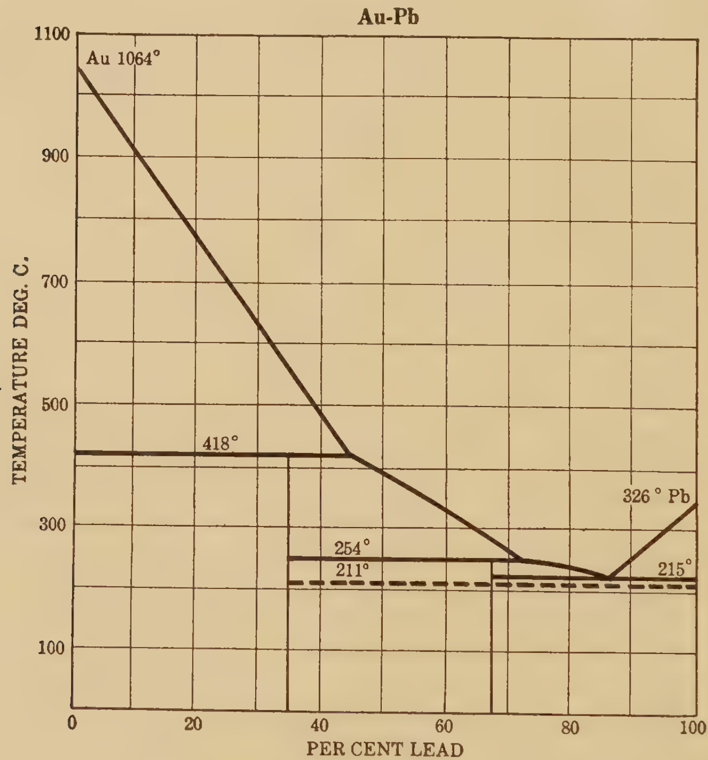

FIG. 47.—Freezing-point curve. Gold-lead.

It is of interest at this point to discuss more fully the question of temperature of cupellation. This term has been used in a vague manner by writers on the subject and has been used to signify generally the temperature of the air of the muffle, either at the side or just above the cupel, or that of the interior of the cupel. Due to the heat of combustion of the lead,

[1] VOGEL, R., *Zeit. Anorg. Chem.*, vol. 45, p. 17, 1905.

neither of these temperatures is the true temperature of cupellation. The actual temperature[1] of cupellation involves experimental difficulties, since the protective tube of the thermocouple in almost any form is rapidly destroyed by the corrosive action of the litharge. As already stated, three temperatures may be considered during cupellation: (1) the temperature

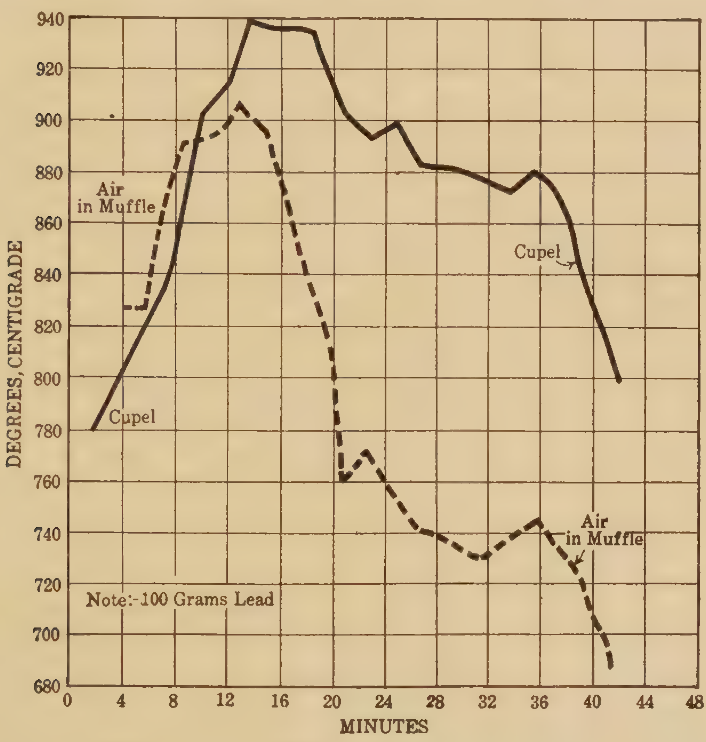

FIG. 48.—Temperature curve—difference in temperature between air and lead.

of the cupelling lead; (2) the temperature of the muffle as determined by that of a blank cupel, adjoining the one containing the lead; and (3) the temperature of the air immediately surrounding the cupel. This is invariably lower than the first two temperatures, which accounts for the low-temperature figures that have been assigned to the cupellation process. It is to be noted that there is an air draft through the muffle

[1] FULTON, C. H., O. A. ANDERSON, and I. E. GOODNER, *Western Chem. Met.*, vol. IV, p. 31. Consult for methods of temperature determinations of cupellation.

during cupellation, cold air constantly entering at the mouth of the muffle, so that the air in the muffle does not attain the temperature of the muffle walls. The actual air temperature is also probably somewhat lower than the thermocouple junction shows, since this absorbs heat radiated from the muffle walls more rapidly than the air. Figure 48 shows the two temperature curves, one, the actual temperature of the cupelling lead, and the other, that of the air in the muffle, close by and at a level with the top of the cupel. The general form of the curve is due to fluctuations of temperature in the muffle, caused by firing and attempts to regulate the temperature, by draft and otherwise. It will be noted that the temperature of the cupel rises rapidly after oxidation has commenced, attaining a maximum of 940° C. and then falling as the muffle cools. The interesting fact is the difference between the temperatures of the air in the muffle and the cupel, which is greatest during the period of active oxidation. The maximum difference is 145° C. The lead "froze" or was covered over with a coating of PbO, preventing further cupellation at 802° C, the air in the muffle being then at 675° C. The actual minimum temperature of cupellation in this case was, therefore, 802° C., 127° higher than the air temperature.[1]

Experiment.—To determine the temperature of the "opening or uncovering" of the button, *i.e.*, the beginning of cupellation, and the "freezing" of the button, *i.e.*, where cupellation is stopped by the formation of PbO which is not absorbed.

In this experiment, 134 g. of lead were used. The presence of gold or silver has no influence on these critical temperatures, as the melting point of the alloys is usually far below the "uncovering" temperatures and the precious metals form no oxides which would complicate matters. The influence of such metals as copper will be referred to farther on. The set was run with a blank, at the same temperature as the cupel before the lead was added. Figure 49 gives the curves plotted as before. The results show that the button begins to "uncover" at 800° and 804° C. and begins to "freeze" at 804° and 788° C. These are the actual cupel temperatures. A repetition of the experiment in the same cupel shows uncovering at 832°, 829°, and

[1] In order definitely to prove the difference in temperature to be due to the oxidation of the lead, a set was run in which the lead in the cupel was covered by a clay dish luted on, practically preventing oxidation. In this instance, the muffle and cupel were at nearly the same temperature for the space of an hour, first one and then the other being a little higher.

834° C. and a freezing at 850° C. Other results show the beginning of uncovering at 797° C. and completely open at 805° C. Another shows an opening to occur at 811° C. Another shows an uncovering at 826° C.; another experiment, at 809° C. In general, the opening temperatures and freezing temperatures are near each other, as is to be expected in so far as the two are, in the absence of any silica, practically the result of the same process. The freezing temperature, however, may be somewhat higher or lower, for a number of reasons developed below. These critical temperatures are of importance in so far as they mark the minimum possible temperature of the beginning of cupellation.

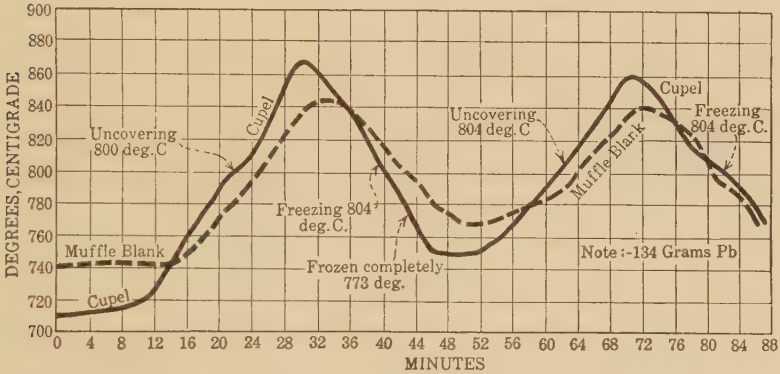

Fig. 49.—Temperature curve during cupellation showing "opening" and "freezing of button."

From the curves it will be noted that as soon as the button uncovers, there is a sharp rise in the temperature of the lead whether the muffle temperature rises or not, due to the oxidation of the lead. In the curves where the muffle blank and the cupel were at the same temperature before the dropping in of the lead, the oxidation raises the cupel temperature from 20° to 150° C. above that of the muffle dependent upon the rate of oxidation, *i.e.*, the air supply. Since it has been well established that the chief cause determining the loss of precious metal by absorption and volatilization is the temperature, it is at once apparent that for careful work the air supply of the muffle is just as important as a regulation of the temperature of the muffle itself. In Fig. 49 the cupel temperature does not rise greatly above the muffle temperature. This is due to the fact that, just as soon as the lead had opened, the furnace was again cooled in order to get a

determination of the temperature of the freezing, thus preventing the attainment of maximum oxidation.

What determines the uncovering and freezing of the buttons? It would appear, at first sight, that the critical temperature of uncovering and freezing is the melting point of litharge, in so far as the melting of the cover of oxide and its absorption by the cupel would naturally mark the "opening." Recent and accurate determinations of the melting point of pure litharge give 906°[1] and 884° C.,[2] with the latter probably the figure to be preferred. In these researches it is noted that before the melting point is reached there is a decided soft and pasty stage, which is ascribed to the marked volatilization of PbO from the solid state. This volatilization begins just below 800° C.[3] and is a function of the area exposed and the temperature. As in the case under consideration, the film of PbO on the button gives probably the greatest area in relation to volume possible, this volatilization is an important factor in the uncovering of the button, in the case of the absence of silica or borax, and the practical ceasing of this volatilization marks the freezing of the button. It will be noted that all the temperature determinations of the opening and freezing are well below the melting point of litharge. It is here self-evident that when a button is put into a cupel whose temperature is 900° C. and above, the temperature at which opening is observed has no special significance.

Lead buttons from crucible assays practically always have adhering to them small amounts of siliceous slag, and the bone ash at times contains minute quantities of SiO_2. When the lead button melts in the cupel, this slag and fine loose bone ash go to the surface into the litharge film. According to the research of Mostowitsch on the lead silicates,[4] the silicates—$6PbO.SiO_2$, $5PbO.SiO_2$, and $4PbO.SiO_2$—are thinly fluid at 794°, 796°, and 726° C., respectively. The percentage composition of these silicates is as follows:

Silicate	Lead Oxide, Per Cent	Silica, Per Cent
$6\ PbO.SiO_2$	95.68	4.32
$5\ PbO.SiO_2$	94.86	5.14
$4\ PbO.SiO_2$	93.66	6.34

[1] Doeltz, O., and Mostowitsch, W. *Metallurgie*, vol. IV, p. 290.
[2] Mostowitsch, W. *Metallurgie*, vol. IV, p. 468.
[3] Doeltz, O., and C. A. Graumann, *Metallurgie*, vol. III, p. 408.
[4] Mostowitsch, Will am, *Metallurgie*, vol. IV, p. 647.

It is evident that when the very small amount of litharge which forms the film is considered, minute quantities of silica only are necessary materially to lower the opening temperature of the button. From these facts it follows that the opening or uncovering temperature is not a fixed temperature but will depend upon the following factors:

1. The presence of silica in a condition to combine with lead (very probably, also, of borax). Where this silica comes from has already been mentioned.

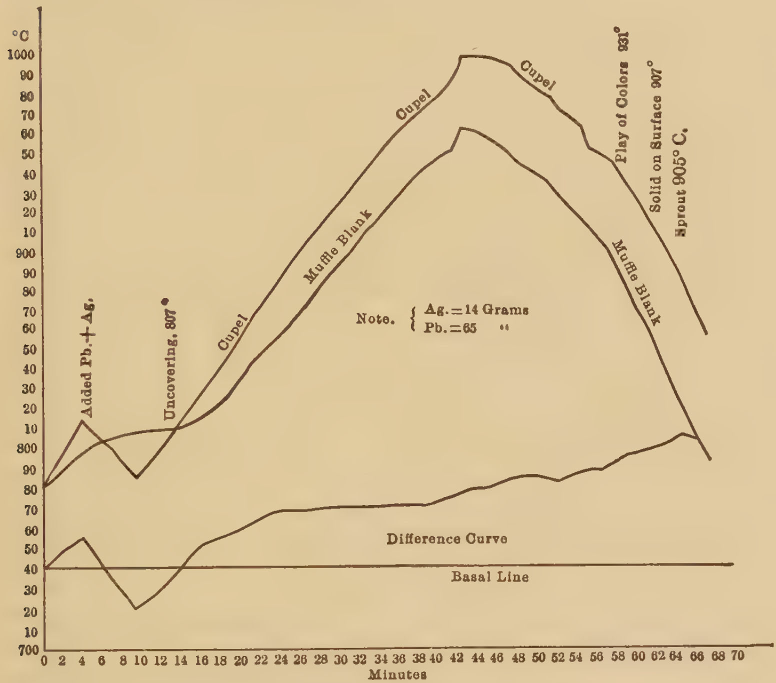

FIG. 50.—Curve showing temperature during cupellation of Pb-Ag.

2. The vaporization of solid litharge. As the rate of vaporization depends upon the temperature, and the relation of area exposed to volume present, a button with a thick covering will not open at a temperature as low as one with a thin covering. This can be demonstrated by placing a button in the cupel at a temperature below 700° C. and permitting it to form a heavy film of PbO, then raising the temperature to the usual uncovering point and placing another button into a second heated

cupel. The last button will uncover first, as its thinner cover of litharge will vaporize in less time.

3. The presence of foreign metals in the lead, such as copper, iron, etc., will raise the uncovering temperature. This is a frequently observed fact, and the reasons for it are practically obvious. If the temperature of the cupel at the moment of uncovering could remain fixed, the increase in the oxidation of the lead would very soon balance the vaporization at that temperature and the button would again freeze, but it has already been noted that a very sharp rise in temperature at once occurs automatically, *i.e.*, independent of the muffle, due to the rapid oxidation of the lead; this effects a marked increase in vaporization, keeping the button open, and soon, in most instances, the temperature of the button itself passes to and beyond the melting point of litharge (884°) and cupellation proceeds rapidly. Cupellation, however, can seemingly be carried on below the melting point of litharge, as Figs. 49 and 50 will show. The particles of litharge formed on the surface of the button, though solid, are pasty and capable of being absorbed by the cupel, or the surface of the cupelling lead being the area of the most active oxidation is at or above the temperature of melting litharge, which the thermojunction at the bottom of the lead does not indicate.[1]

In one experiment, containing considerable silver, it was noted that very near the end of the cupellation when the amount of silver was large and that of lead small, the button was cupelling at an indicated cupel temperature of 750° C., the button then solidified and proved to be a lead-silver alloy. The temperature of 750° evidently did not represent the surface temperature of the button as was indicated by the brightness of the PbO specks formed; *i.e.*, the amount of heat liberated by the small amount of lead oxidized was insufficient to make any material impression on the thermojunction.

The "Freezing" of the Button.—When the temperature of the muffle falls so that the heat of oxidation of lead is no longer

[1] In an experiment to shed light on this point, 70 g. of pure PbO were placed in a cupel and heated to 815° C. for 20 min. The litharge showed vaporization, but none was absorbed by the cupel. In a duplicate experiment, the temperature was raised to 883° C. just below the melting point, and while the litharge did not melt, all of it was rapidly absorbed by the cupel. In the first case, the mass of litharge was sintered. Absorption thus probably occurs in the "pasty" stage mentioned.

enough to keep its temperature such that the rate of vaporization is in excess of the rate of oxidation, the molten button will become covered by a film of litharge and cupellation ceases.

"Feathers" are crystals of solid litharge sublimed from the vapor and deposited on the cupel walls. That the cupel walls are invariably cooler than the cupelling lead is self-evident. Feathers will, therefore, form when the temperature of the cupel wall is below or near that of uncovering. They will not form above about 820° C. The cooler wall and that on which feathers most usually form is that toward the muffle mouth, due to the direct impingement of cooler air currents. These feathers form the best guide to the temperature of cupellation ordinarily available. During their formation, the actual temperature of the cupelling lead is usually from 840° to 900° C., although it may be appreciably higher if the oxidation is rapid. The rapidity of the oxidation depends largely on the air supply, and this heavy air current striking the cupel may cool the walls sufficiently to cause a heavy sublimation of feathers, although the true temperature of cupellation, *i.e.*, that of the button, may be unduly high.

Résumé.—From the foregoing, it appears that the uncovering of the button occurs at from 800° to 840° C., dependent on several factors, and that the actual *minimum temperature* of cupellation may be placed at about 850° C. but usually rises above this, *i.e.*, independent of the muffle, frequently to 930° and 940°, unless the muffle temperature is lowered after uncovering. The necessary finishing temperature is, however, higher than 850° C.

Experiment.—To determine the phenomena incident to the "finishing" of a cupellation containing silver, *i.e.*, that of "surfusion," "sprouting," freedom of the silver bead from lead, temperature necessary to finish, etc.

It has frequently been noted that a cupellation containing silver and gold, or both, could seemingly be "finished," *i.e.*, all the lead eliminated therefrom, when the temperature of the muffle was well below that of the melting point of silver, *i.e.*, 962° C., or that of the gold-silver alloy. From the foregoing, it is evident that the temperature of the muffle is not by any means the same as that of the cupellation. Roberts-Austen[1] quotes Dr. Van Riemsdijk, stating that

[1] "An Introduction to the Study of Metallurgy," 5th ed., p. 50, citing *Ann. chim. phys.*, vol. XX, p. 66, 1880.

. . . he observed that a globule of gold or silver in a fused state will pass below its solidifying point without actually solidifying, but the slightest touch with a metallic point will cause the metal to solidify and the consequent release of its latent heat of fusion is sufficient to raise the globule to the melting point again, as is indicated by the brilliant glow which the button emits.

Rose[1] also quotes the same author, and it is evident that the gold and silver globules mentioned are derived from cupellation.

Six sets of experiments were carried on in this connection, some of which are plotted in Figs. 50, 51, and 52. It is evident from these figures that surfusion unquestionably occurs, and in a most marked manner, the greatest degree of surfusion noted being 77° C. All of the buttons "sprouted," *i.e.*, showed cauliflower-like growths of silver on final solidification. This sprouting has always been considered a sign of purity of the silver,[2] particularly pointing to the absence of lead.

In order to test this point, some of the silver buttons from the experiments were very carefully examined for lead in quantities of a gram and showed but traces of it, quantities not determinable. Some showed minute quantities of copper. In effect, they were all "fine silver." The surfusion is, therefore, very real. In the authorities cited on surfusion, the statement is made that on solidification from surfusion, the "flash" of the button occurs, showing the raising of the temperature to the melting point of the silver. H. M. Howe[3] states:

Once freezing sets in (in the surfused metal or alloy) the heat which it evolves raises the temperature toward, and more often quite to, the true freezing point, where it remains during the remainder of the freezing.

In experiments carried on with the following quantities of silver, 10, 14, 18, 30.4, and 30 g., the "flash" was not observable, either by the eye or by any actual rising deflection of the galvanometer pointer, although a repeated and careful search was made for this. In order to determine whether the size of the button had any influence on the flashing, various amounts of silver, beginning with 350 mg. and varying by 50 up to 850 mg., were

[1] "Metallurgy of Gold," 4th ed., p. 598.

[2] Rose, T. K. "Metallurgy of Gold," p. 477; Collins, H. F. "Metallurgy of Silver," p. 2, 1900; Schnabel, C. "Metall-Huettenkunde," p. 605, 2nd ed., 1901. Louis' translation, 1st ed., p. 578.

[3] "Iron, Steel and Other Alloys," p. 20, 1903.

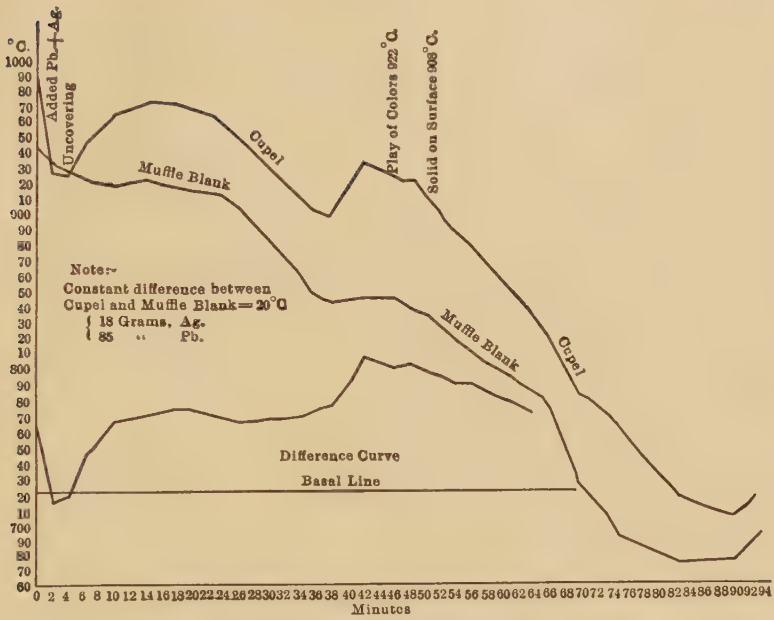

FIG. 51.—Curve showing temperature during cupellation of Pb-Ag.

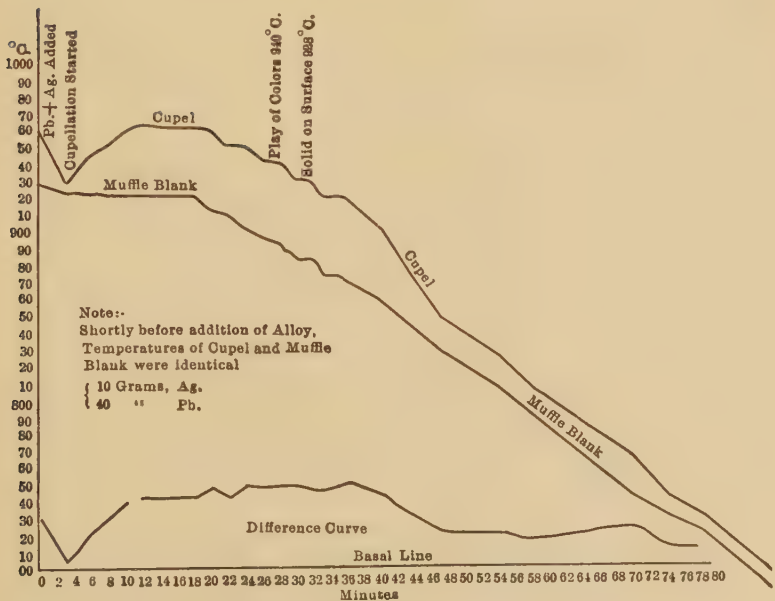

FIG. 52.—Curve showing temperature during cupellation of Pb-Ag.

cupelled so as to finish with surfusion. It was found that the beads up to and including 650 mg. flashed markedly, that of 700 mg. faintly only, and those above showed no flash.

If the differences in temperature between the cupelling alloy and the muffle blank at any time interval be plotted as ordinates from a basal line, it is readily shown by the different curves that the greatest difference occurs at the close of the cupellation—in some instances, just as the last of the lead oxidizes (play of colors). The differences noted show the marked evolution of heat at the finishing of the cupellation and are due to the release of the latent heat of fusion. In the case of the large buttons, however, this does not seem to be sufficient to cause an actual rise of temperature in the cupel, when the muffle temperature is actively sinking, as was the case in experiments shown by Figs. 50, 51, and 52. As already stated, however, no flash was observable to the eye in the larger silver buttons, nor did the galvanometer indicate it, as surely might be expected. The lag or time interval between the occurrence of a temperature and its recording by the galvanometer is not great when an iron protective tube is employed. This is shown very plainly by the marked "jogs" in the cupel curves when the lead alloy is added to the cupels (Figs. 51 and 52). The lowest finishing temperature found showed surfusion extending to about 885° or 77° C. below the melting point of silver. The temperature indicated by the "muffle blank," which at the start was 10° below the cupel, was 845° C. The last of the lead went off from the cupel at 910°. This represents about the minimum finishing temperature, judging by the general appearance of the cupellation. It is to be noted, however, that this finishing temperature is reached automatically in the cases where the muffle temperature is such as to afford uncovering of the button and prevention of freezing, *i.e.*, approximately 830° to 840° C. on the average, in the case of pure lead buttons. One experiment was carried out in which the cupelling lead alloy showed a muffle temperature of 750°[1] not far from the end of cupellation, but at this temperature the button solidified into a lead-silver alloy. The approximate composition of the silver-lead alloy freezing at this temperature is 70 per cent Ag, 30 per cent Pb.

[1] For an explanation of this seemingly low cupellation temperature, see p. 117.

Résumé.—It appears from the foregoing that

1. In the case of the lead buttons not containing any appreciable amount of copper or iron, etc., a *muffle temperature* of at least 800° C. or, better, one of 850° is required to insure uncovering or to start cupellation.

2. This temperature may be lowered to about 770° C. during the oxidation of the greater part of the lead.

3. Toward the end of the cupellation or the finishing, in case of silver, it must again be raised to about 830° C. in order to get a pure silver button.

4. The *actual* temperature of the cupelling lead is always appreciably higher than the *muffle temperature.*

5. The *actual* finishing temperature of the cupellation cannot safely be carried below about 910° C.

6. The greatest observed surfusion of silver was 77° C. and this is probably very near the maximum.

7. Silver beads finishing with surfusion are free from lead.

8. "Feathers" or crystals of sublimed litharge on the cupel are an indication of the proper cupellation temperature, provided the air draft is not excessive.

9. It is just as essential to regulate the air draft of the muffle as its temperature.[1]

Where very accurate cupellation work is required, such as in bullion assaying and where the amount of work justifies it, a furnace designed for close temperature and air control is practically essential. In view of the recent improvement in electrically heated furnaces, in which temperatures can be *rapidly* and accurately controlled and the muffle heated uniformly, practically eliminating the thermal gradient, a furnace of this type would seem best adapted for the work.

Influence of Base-metal Impurities

When the lead buttons are contaminated with base metals, such as copper, the temperature of cupellation must be higher in order to prevent freezing. The reason for this is readily apparent when the freezing-point curve (see Fig. 53) of the lead-copper series of alloys is inspected.[2] The freezing point of an alloy containing 10 per cent Cu and 90 per cent Pb is 900° C.

[1] The effect of air on cupellation losses was thoroughly investigated by J. T. King, Univ. Toronto, School Eng. Res., *Bull.* 6, Sec. 15, 1926.

[2] Friedrich, K., and M. Waehlert, *Met. u. Erz* vol. 10, p. 578, 1913.

While the original copper percentage in the lead button may be quite small, the copper does not oxidize so readily as the lead and tends to concentrate in the button, rapidly raising the melting point of the alloy.

For the removal of copper in cupellation, the ratio of Pb to Cu should be at least 200:1 and preferably more. Even then, Cu will be retained by the silver and gold in small amounts. If it is less than this, a considerable amount of copper is very apt

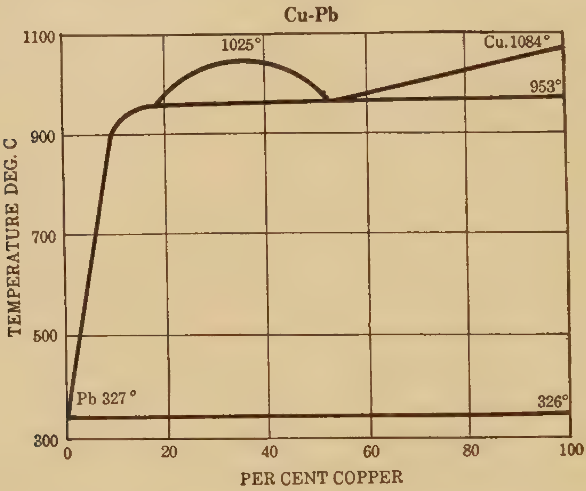

FIG. 53.—Freezing point curve. Lead-copper.

to be retained with the silver and gold. In order to cupel at all, the ratio of Pb to Cu must be at least 20:1. In general, buttons to be cupelled should be free from base-metal impurities. If they are unavoidably present in the button from the crucible assay, the base metals should be removed by scorification before cupellation.

Impurities in lead buttons are detected by the behavior of the button. Zn, As, Sb, and S tend to make the button brittle when hammered; iron and copper, etc., tend to make it hard. PbO in the lead button makes it brittle. PbO is often found in lead buttons that have been produced at a too low temperature. Where the gold and silver contents of the lead button approach 30 per cent of its weight, it is brittle.

Impurities in the lead button will not always be indicated, however, by brittleness or hardness; without these characteristics,

impurities may still be present in sufficient amount to cause loss. All impurities do not cause like amounts of loss in cupellation. The loss due to the presence of impurities is chiefly in absorption by the cupel and comparatively small by volatilization.

The accompanying table[1] shows the influence of impurities. Twenty-five-gram lead buttons were cupelled, containing 1 g. of the impurity specified, 4 mg. Ag, and 1 mg. of Au. The temperature of cupellation was 1000° C., in order to prevent freezing as a result of impurity.

Table XX.—Influence of Impurities

Impurity	Loss of gold, per cent	Loss of silver, per cent	Remarks
None	1.2	11.8	
Tin	2.0	13.9	
Arsenic	3.9	16.3	
Antimony	5.3	13.3	
Zinc	9.3	17.6	
Cadmium	3.5	13.1	Most of this loss, even with Te and Se, is cupel absorption
Iron	4.0	16.6	
Manganese	13.6	24.3	
Molybdenum	11.0	26.2	
Vanadium	7.7	21.7	
Copper	10.0	32.6	
Bismuth[1]	21.8	27.9	
Thallium	23.1	34.4	
Tellurium	55.8	67.9	
Selenium	54.1	64.5	

[1] Doubtful.

The high losses are due, in part, to the high temperature employed. The table really gives the relative influence of the impurities. Bismuth has been used in place of lead for cupellation. While in the table bismuth is stated to be the cause of a very heavy absorption, this is not substantiated by other research.[2] When it is present in the lead button, it tends to concentrate during the cupellation and is removed by oxidation toward the last of the operation. Some of it is very apt to be retained by the precious metal bead. Cupellation may be carried

[1] Rose, T. K., *Jour. Chem. Met. Mining Soc. S. Africa*, vol. V, p. 165, 1905.

[2] Sander, K., *Berg- und Huettenmaennische Zeitung*, vol. 62 p. 81, 1903; see, also, *Mineral Ind.*, vol. XII, p. 244.

on with bismuth, but the absorption is much higher.[1] The presence of bismuth in the cold cupel may be recognized by the fact that the place which the silver button occupies is brown and surrounded by concentric rings of a yellow and blackish-green color. Copper colors the cupel from a dirty green to a black, dependent on the amount of copper.

Tin, arsenic, zinc, cadmium, iron, and manganese cause scoria to form on the cupel, due to the formation of oxides which are not readily absorbed. Iron causes a dark coloration of the cupel. Antimony in considerable quantity causes the cupel to check and crack. The same may be said of copper.

Copper.—This metal is oxidized with more difficulty than lead, the Cu_2O forming by aid of the action of PbO; however, Cu_2O, again coming into contact with metallic lead, is reduced to Cu and in this way is persistent toward the end of the cupellation, although a large excess of Pb over Cu is present, and finally some

TABLE XXI.—COPPER IN CUPELLATION OF SILVER AND GOLD
Temperature of Air in Muffle, 775 C.

Silver, milligrams	Lead, grams	Copper, grams	Percentage of copper in lead	Percentage of loss	Ratio Pb: Cu
202	10	0.0101	0.1	1.05	1,000:1
203	10	0.0202	0.2	1.08	500:1
202	10	0.0303	0.3	1.29	333:1
202	10	0.0404	0.4	1.45	250:1
204	10	0.0500	0.5	Cu retained	200:1

Gold, milligrams	Lead, grams	Percentage of copper in Pb	Percentage of loss		Ratio Pb: Cu
202	10	None	0.155	All contained copper on finishing	
202	10	0.1	0.19[1]		1,000:1
201	10	0.2	0.20		500:1
200	10	0.3	0.13		333:1
201	10	0.4	0.165		250:1
202	10	0.5	0.250		200:1

[1] Actual losses; copper retained, 0.16 per cent. Gold about the same weight as before cupellation.

[1] SMITH, E. A. *Jour. Chem. Soc.*, vol. 65 p. 624, 1894.

remains with the Au and Ag. The loss of silver during the cupellation is due mainly to absorption, in large part as oxide. This oxidation of the silver in the presence of much lead is not to be ascribed to the action of atmospheric oxygen but rather to "oxygen carriers," such as PbO, Cu_2O, etc. It is very probable that Cu_2O acts peculiarly in this manner and that the high absorption noticed when Cu is present is due to this fact. It is to be noted that losses in silver occur toward the end of the cupellation and occur in great part just before finishing; the small black-green ring, surrounding the place where the silver bead rests, locates most of the silver. It is the concentration of the copper, silver, and gold that causes the high absorption. Lodge[1] shows the influence of small amounts of copper on the cupellation of silver and gold.

Gold is more retentive of copper than silver. It is to be noted that even with a ratio of 200 Pb:1 Cu, it is not possible to remove the last trace of copper, and beads obtained from mattes and heavy copper ores should be examined for copper; otherwise, the silver results may be too high. Retained copper in these silver beads will compensate for loss of silver, but the amount retained is so variable that this error cannot be considered to compensate the loss.

Tellurium.—Tellurium has a great affinity for gold and silver, and if present in an ore in any appreciable amount, some of it will go into the lead button with the gold and silver and thus have its influence on the cupellation. It tends to concentrate during the cupellation and is with difficulty removed by oxidation. When the tellurium present in the lead button is more than 15 per cent of the gold and silver weight, the beads resulting from cupellation have a dull and frosted appearance. Larger amounts than this cause the beads to divide and split up in the cupel. F. C. Smith[2] shows the influence of tellurium on the cupellation as follows, these results being confirmed by J. C. Bailar[3] and others:

[1] "Notes on Assaying," p. 143 *et seq.*

[2] "The Occurrence and Behavior of Tellurium in Gold Ores," etc., in *Trans.* A. I. M. E., vol. XXVI, p. 495.

[3] *Western Chem. Met.*, vol. I, p. 119.

TABLE XXII.—TELLURIUM IN CUPELLATION OF GOLD AND SILVER
Cupelled with 12 g. of Lead

Bullion, milli-grams	Containing		Te milli-grams added	Loss by absorption, per cent		Loss by volatilization, per cent	
	Au	Ag		Au	Ag	Au	Ag
29.8	24.76	5.04	5.0	13.44	27.08	5.65	0.69
28.45	23.64	4.81	15.0	34.22	35.78	5.28	1.75
22.17	18.42	3.75	15.0[1]	29.85	32.01	11.92	17.95

[1] Selenium instead of tellurium.

Note the similar effect of selenium.

Antimony.—The presence of antimony causes increased losses by absorption, although its effect is not so pronounced as that of copper or tellurium. During the cupellation, litharge and antimony combine to form antimoniate of lead, which, if present in considerable amount, may cause the formation of scoria on the cupel. Small amounts of antimony tend to remain with the gold and silver, as with copper and tellurium.

As a guide in cupellation, the following scale of color temperatures is given:[1]

	Degrees, Centigrade
Lowest red visible in the dark	470
Dark blood red or black red	532
Dark red, blood red, low red	566
Dark cherry red	635
Cherry red, full red	746
Light cherry, light red	843
Orange	900
Light orange	941
Yellow	1,000
Light yellow	1,080
White	1,205

CUPELLATION IN CUPELS OF DIFFERENT MATERIAL

The cupel material has a decided influence on the progress of a cupellation. What has preceded refers more particularly to bone-ash cupels. In cupels with a magnesia base, the process as regards temperature differs somewhat, due to the different thermal properties of the two types of material. The following differ-

[1] WHITE and TAYLOR, *Trans.* Am. Soc. Mech. Eng., vol. XXI, p. 628; HOWE, H. M., *Eng. Mining Jour.*, vol. LXIX, p. 75.

ence in thermal properties may be noted.[1] Bone-ash cupel, mean specific heat between 15° and 100° C. is 0.185. Magnesia cupel, mean specific heat for same temperatures is 0.215. A bone-ash and magnesia cupel of identical volumes weigh, respectively, 22 and 29 g. The heat conductivity of magnesia cupels is very much greater than that of bone-ash cupels. When the two types of cupel are heated to 90° C. in a steam bath, at the end of 14 min. the magnesia cupels are at 90° C. and the bone-ash cupels at only 60° C. During cupellation of lead, at the end of 6 min. from the addition of the button, the magnesia cupel showed practically the same temperature in the cupelling lead as in the bottom of the cupel, *viz.*, 920° C., while the bone-ash cupel in the same muffle showed a temperature of 990° C. for the cupelling lead and only 932° C. in the bottom. The total heat capacity of a magnesia cupel is more than 50 per cent greater than that of a bone-ash cupel of the same volume, so that on cooling the two types of cupel the magnesia cupel retains a higher temperature somewhat longer than the bone-ash cupel in spite of its greater diffusivity of heat. From these data, the reason of the difference in behavior of magnesia and bone-ash cupels during cupellation is apparent. It will be noted: (1) that in magnesia cupels the lead is less bright and, hence, at a lower temperature than in bone-ash cupels, although the muffle temperature is the same. This is due to the fact that the extra heat generated by the combustion of the lead is diffused as rapidly as generated by the superior diffusivity of the magnesia cupel and, therefore, cannot serve to raise the temperature of the lead, as is the case in the bone-ash cupel. Hence, for the same "muffle temperature," the actual cupellation temperature of the lead in the magnesia cupels is 50° to 60° C. lower than in the bone-ash cupels. To this fact is due the lower loss of precious metal in magnesia than in bone-ash cupels when used side by side. In the discussion of cupellation temperature it will have been noted that with bone-ash cupels, if once the muffle has attained a temperature sufficiently high to cause the uncovering of the button, the rise in temperature of the lead due to its oxidation is sufficient to carry the cupellation to a finish provided the muffle temperature is not lowered at the end of the operation. This is not the case with magnesia cupels for now obvious reasons, and

[1] Bannister C. O. and W. M. Stanley, "Thermal Properties of Cupels," I. M. M., *Trans.* vol. XVIII, p. 439, 1909.

it will be necessary to raise the muffle temperature toward the end of the operation or, what amounts to the same thing, push the cupel to the hotter part of the muffle. Assayers who are used to bone-ash cupels, therefore, have some difficulty at first due to freezing of buttons when using magnesia cupels.

2. Magnesia cupels retain a higher temperature longer than bone-ash ones when withdrawn from the furnace or moved to the cool part of the muffle, and, hence, silver buttons show a lesser tendency to sprout, due to the slow cooling they undergo.

The lead in magnesia cupels seems to open somewhat more readily and cupels slightly faster than in bone-ash cupels.

The accompanying tables give data of results obtained by bone-ash and magnesia cupels on pure silver and on a copper matte.[1]

TABLE XXIII.—COMPARISON OF BONE-ASH AND MAGNESIA CUPELS ON C. P. SILVER CUPELLED WITH 10 g. SHEET LEAD

Amount of silver taken, milligrams	Bone-ash cupels. Silver bead, weight, milligrams	Magnesia cupels (morganite). Silver bead, weight, milligrams
5	4.85	4.80
10	10.00	10.00
15	14.72	
20	19.30	
25	24.41	
15	14.36	14.50
20	18.92	19.52
25	23.84	
5	4.94	4.89
10	9.68	9.86
15	14.70	14.80
20	19.98	19.68
25	24.60	24.84

The sheet lead used contained a little silver. Cupellation, in most cases, was carried out with feathers. It is to be noted that when low finishing temperatures are employed, as is apt to be the case with magnesia cupels, the beads may retain small amounts of other metals, notably lead,[2] to which may be due, in some cases, the higher results obtained.

The assays given in the table were made by the excess-litharge method. The average result stated in ounces per ton is as follows:

[1] By O. A. Anderson and C. H. Fulton, S. Dak. School Mines, laboratory.

[2] LIDDELL, D. M., *Eng. Mining Jour.*, vol. LXXXIX, p. 254.

Table XXIV.—Comparison of Bone-ash and Magnesia Cupels on a Copper Matte

Number	Weight of lead button, grams	Matte taken, A. T.	Bone-ash cupels			Magnesia cupels (morganite)		
			Au + Ag	Ag	Au	Au + Ag	Ag	Au
1	18	0.05	11.0	10.38	0.62	13.0	12.37	0.63
2	24	0.10	21.12	19.80	1.32	23.3	22.02	1.28
3	28	0.15	31.30	29.22	2.08	27.2	25.17	2.03
4	30	0.25	56.10	52.82	3.28			
5	14	0.05	11.0	10.36	0.64	12.50	11.82	0.68
6	18	0.10	21.8	19.48	1.32	27.0	25.67	1.33
7	25	0.20	44.5	41.90	2.60	47.0	44.37	2.63
8	10	0.05	10.9	10.30	0.60	11.2	10.58	0.62
9	14	0.10	21.3	20.10	1.20	22.0	20.70	1.30
10	31	0.20	42.6	40.04	2.56	43.1	40.52	2.58
11	24	0.25	53.0	49.75	3.25	53.6	50.28	3.32

for bone-ash cupels, gold 12.86 oz., silver 202.67 oz.; for magnesia cupels, gold 13.16 oz., silver 222.76 oz. These results are uncorrected assays, *viz.*, do not include the slag or cupel absorption. In practice, it was found necessary to make these corrections to obtain concordant results. It will be noted that the magnesia cupels give higher results on gold and very much higher results on silver. This last is, without question, due, in large part, to the retention of copper by the beads and calls for caution in the use of magnesia cupels on this type of material.

Portland-cement Cupels.—During cupellation, portland-cement cupels act very similarly to bone-ash cupels. The loss is somewhat higher than in bone-ash cupels. The accompanying table gives losses in portland-cement cupels and bone-ash cupels and those made of one-half of each material. The temperatures are average temperatures during cupellation, from the opening of the button to the "blick." With about 20 g. of lead were cupelled 100 mg. of silver.[1] The temperatures were measured by inserting a thermocouple into a hole bored beneath the bowl of the cupel. They, hence, represent a temperature which is a mean between that of the cupelling lead and a muffle "blank" cupel.

[1] Holt and Christensen, "Experiments with Portland Cement Cupels," *Eng. Mining Jour.*, vol. XC, p. 560.

TABLE XXV.—CUPELLATION LOSSES WITH DIFFERENT TYPES OF CUPELS

Average temperature, degrees centigrade	U. S. portland cement, loss per cent	R. D. portland cement, loss per cent	One-half cement, one-half bone-ash, loss per cent	Bone ash, loss per cent
915	1.30	1.34	1.21	1.26
925	1.81	1.72	1.54	1.70
945	2.53	2.56	2.42	2.42
965	3.37	3.42	3.05	2.96

Another test to determine the relative absorption of bone-ash and cement cupels[1] gave the following results: On 10 mg. silver with 15 g. lead, at an orange heat (very high), cement cupels showed 6.64 per cent absorption and bone-ash cupels 6.38 per cent. At a light-cherry heat, cement cupels showed 4.91 per cent and bone ash 4.62 per cent absorption. It is to be noted that the percentage absorption, other factors being equal, is dependent on the amount of precious metal cupelled (see p. 199). In using cement cupels, the beads must be carefully cleaned; otherwise, when parting in nitric acid, insoluble silica is apt to remain which will be weighed as gold. The bead on cement cupels is likely to be more flat than on bone-ash cupels. When using bone ash cupels of ordinary porosity, a lead button requires a cupel of slightly greater weight than itself to insure complete absorption: magnesia and cement cupels must be considerably heavier.

[1] MERRITT, J. W., "Cement *vs.* Bone-ash Cupels," *Mining Sci. Press*, vol. C, p. 649.

CHAPTER IX

PARTING AND INQUARTATION

Parting

Parting is the separation of gold from silver by means of acid. In assaying, nitric acid is almost exclusively employed, although sulphuric acid may also be used. The aim is to remove all the silver, together with any base metal that may possibly be present, and to leave all the gold in a weighable condition. To do this requires careful consideration of the following points: (1) the strength or concentration of the acid, (2) the temperature of the acid when used, (3) the ratio of silver to gold in the alloy to be parted, (4) the time of contact, and (5) the relative area exposed to acid, or the thickness of the alloy, which, to some extent, determines the time necessary. The method of washing after parting also demands some attention to detail, to insure the removal of the nitrate of silver formed.

The conditions confronting the assayer in parting bullion samples differ so much from those met in parting the smaller buttons obtained in treating most ores and metallurgical products, that it is best to consider the two cases separately.

In parting bullion samples, the weights of metal are relatively large, and it is of importance to remove the last trace of impurity possible from the gold, the weight of which mainly determines the value of the material under assay. Considering an alloy containing silver and gold alone, if the gold much exceeds half the silver by weight, it protects the silver from the action of nitric acid, making complete separation impossible. If the ratio of silver to gold exceeds 2, hot nitric acid of moderate concentration (say, between one-third and two-thirds concentrated acid with two-thirds to one-third water) will remove the silver and leave the gold in a more or less coherent but soft and spongy condition. If, however, the silver-to-gold ratio exceeds 3, the gold easily breaks up. Formerly, the ratio 3:1 was thought to be an ideal one, the gold forming one-quarter of the total

fineness; hence, the term *inquartation* was applied to the adjusting of this ratio with added silver.

There has been considerable variation in practice as regards the ratio of silver to gold and also in the concentration of the nitric acid used in parting. This is shown in Table XXVI. For practical purposes, any ratio between 2:1 and 3:1 may be adopted for the alloying, but it is risky to go beyond these limits. For general purposes, therefore, the ratio 2.5:1 is recommended, as it leaves a reasonable leeway on either side. For the first acid, a specific gravity of 1.2 is recommended, and either 1.3 or 1.35 for the second, though practice differs. An intermediate wash between the two acids is a decided advantage, although many assayers omit it; the second acid then carries very little silver and may be used for the first acid of a later batch of assays.

For occasional assays of bullion, there is nothing better than the old method of parting in glass flasks or matrasses. The old French flasks were almost egg shaped, with very long necks which prevented the escape of spurting acid when "bumping" takes place; small Erlenmeyer or plain conical or flat-bottomed round flasks may also be employed. When using flasks, the acid is subject to violent bumping after most of the silver has dissolved, so that the gold may be broken up or projected out of the vessel. This is prevented by introducing a fragment of carbon. Formerly, charred peas or peppercorns were used, but a good substitute is battery carbon previously extracted with nitric acid or, better still, Acheson graphite. In flasks regularly used for the purpose, a bit of platinum wire may be fused into the bottom, from which bubbles of gas will rise, as is done in some physical apparatus.

When parting a number of cornets at a time, the standard platinum parting apparatus used at mints is extremely convenient. A number of platinum cups, perforated or slotted at the bottom, are placed in a perforated platinum tray or frame holding 9, 16, or up to 36 cups in small compartments. This frame has a wire handle and is placed in a platinum container, which may be covered with an inverted funnel. Hot acid is poured in, the container is heated, and the tray is introduced and removed for washing by a glass hook; the holes allow of easy circulation and draining of acid and water. Bumping of the acid does not take place in platinum vessels. After the second acid and final washing, the washed gold is carefully dried

TABLE XXVI.—BULLION PARTING PRACTICE

	Ratio, silver to gold	Grams, lead	Milligrams, copper	Strength of nitric acid used: Baumé	Strength of nitric acid used: Specific gravity	Minutes boiling	
Practice at different U. S. mints and assay offices (Dewey).	3	2	10	22 32 32	....	10 10 10	platinum
	2	8	50	32 32	....	10 10	platinum
	2	3	5 to 10	22 32	....	20 20	platinum
	2.5	5	25	27 32	....	10 10	platinum
	2	2	7.5	32 32	....	10 10	platinum
Old San Francisco Mint practice	3	..	....	20 30	....	20 10	flasks
London Mint (Rose)	2.17	4	40	....	1.2 1.22	30 30	platinum two intermediate washes
Old practice	2.75	2	40	....	1.2 1.32		
A. C. Claudet (Bank of England Assayer)	2.5	2	17.5	....	1.16 1.25 1.25	10 20 20	platinum
Rand, South Africa (Loevy)	.....	2 to 6	2.5 to 5	....	1.2 1.3 1.3	10 10 10	flasks
Rand (Johnston)	2.5	.....	....	....	1.2 1.3	10 10 30 30	
Rand	2.2 to 2.5	..	....	....	1.18 1.42	20 20	platinum or silica
Homestake mine	2.5	5	10	....	1.2 1.35	10 10	platinum intermediate wash
E. A. Smith	2.5	..	....	....	1.2 1.35	10 15 15 20	platinum or flasks
Van F. Furman	2.5	4 to 5	....	25 32	1.2 1.27	10 10	
Van F. Furman (fine bullion)	2	..	...	32 32	1.27 1.27		
Vauquelin (1800)	2 to 3	..	....	22 32	....	15 7 20 8	
Chaudet (1835)	3	..	....	22 32	....	20 8 20 10	
Mitchell	2.5+	..	....	....	1.15 1.25	15 12 20	

and then annealed by holding the tray a few minutes in a hot muffle, taking care to avoid heating so strongly that the cornets become welded to the cups. If properly cared for, this apparatus lasts indefinitely; it is, however, expensive, and one disadvantage is the fact that a miscalculated inquartation with the addition of too much silver, causing the breaking up of a button, may contaminate all the other assays in the tray. More than half the cost may be saved by using a pyrex beaker for the containing vessel. There is no apparent reason why pyrex or porcelain should not be used for the perforated cups or tray, but no such equipment is in the market. The cups and tray are, however, sometimes replaced by a frame and cups of fused silica (vitreosil). Tantalum resists the action of hot nitric acid but oxidizes too easily at the temperature desirable for annealing.

When parting in glass, each flask or tube must be separately decanted to remove the acids and wash water; finally, the flask is filled with water to the top, a glazed porcelain crucible or an unglazed "dry cup" is inverted over it, the flask is then turned upside down, and the cornet or fragments allowed to collect in the crucible or cup. By a quick turn of the wrist, the flask can be removed without spilling a drop of water. The excess water is then drained from the cup; the last drops may be removed by a bit of filter paper. The cups are then arranged in a rack, gently dried, and heated in a muffle or over a coal-oil lamp or electric heater. A three-stage electric heater is most convenient for this work; for drying the low heat is used with a thin asbestos board interposed. Sudden heating of cornets while still moist may cause small explosions, which sometimes project part of the gold to some distance. When dry, further heating to a low redness causes the gold to contract gradually and become tough and of a brilliant yellow; it can then be handled with forceps without danger of breakage.

In the case of rich material such as certain gold concentrates, amalgam, and cyanide precipitates, where the doré buttons contain insufficient silver for parting, it is best to run at least three assays. The approximate fineness of the doré button is then obtained by comparison with a set of touch needles. The proper weight of fine silver for bringing the ratio up to 2.5 is then added by cupelling the button wrapped with about 20 mg. copper and 5 g. lead. It is then rolled out thin, annealed, coiled, and parted

in glass or platinum, and a set of proofs may be employed to correct for loss or surcharge.

Buttons from ores and most metallurgical products are best parted in small glazed-porcelain cups or crucibles. Coors' Nos. 0 and 00 high form are very suitable for most ores; larger ones may be used for those high in silver. They are best carried in racks made of sheet iron, having holes punched to fit the cups. The operations of parting, washing, and drying are carried out in these racks; for annealing in the muffle, the cups may be trans-

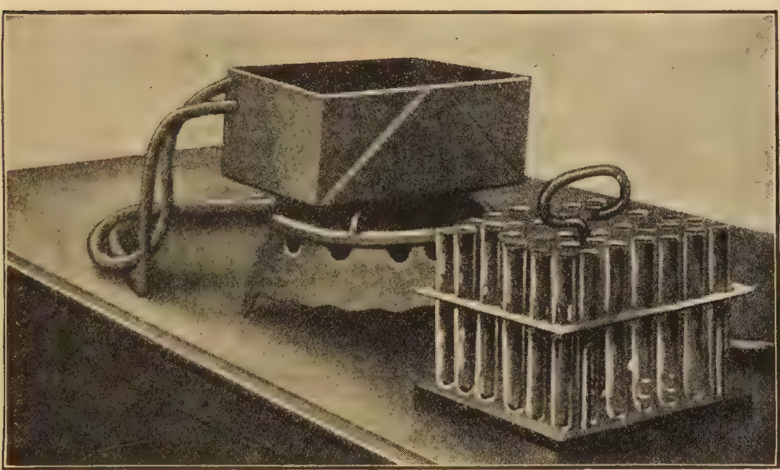

Fig. 54.—Parting bath.

ferred to a cast-iron tray, or the annealing may be done in the same rack over a kerosene lamp or an electric heater with open coils. The cups should be heated to incipient redness, so that the smallest gold particles change from black to yellow. They may then be transferred to a cold rack to be taken to the balance weighing room.

Some assayers prefer to use small flasks or matrasses, or test tubes; the latter may be conveniently set in a crate or container with crosspieces to separate the tubes. This can be filled with hot water to hasten action, and, as a rule, it is advisable to preheat the acid somewhat before introducing the buttons.

Owing to the relative smallness of the gold left to be weighed, the removal of the last trace of silver is generally less important than in the case of bullion.

Where silver is largely in excess, quite dilute acid is sometimes used. At one Montana works, in parting the large silver buttons obtained from such material as anode mud or blister copper, it was the rule to use large porcelain crucibles with acid containing only 5 per cent by volume of strong nitric acid and to warm this only slightly. Dr. Edward Keller, also working with Montana copper products, recommends 10 per cent acid, and the rack of test tubes (Fig. 54) is at once placed in a bath of boiling water.

Treated in this way the gold almost invariably remains in the form of a coherent bead, even from an alloy as low as 1 part gold in 500 silver.

In the case of ores, great variation exists in the practice. Furman recommends acid of 13° Bé., or sp. gr. about 1.1. In "Rand Metallurgical Practice," one treatment with "40 per cent" acid is recommended (*i.e.*, 2 volumes: 3 of water, or sp. gr. about 1.16); McArthur Johnston in "Rand Assay Practice" advises 1:3 by volume, dropping the flattened beads into warm acid. L. S. Austin uses the same strength, followed by a few drops of stronger acid, both boiled. At the Homestake, acid of sp. gr. 1.08 is first used, followed by sp. gr. 1.20. Clennell uses 1:7 heated 15 min., then a wash, followed by strong acid (3:1 or sp. gr. 1.32) boiled 30 min. He states that beads of 60 to 80 mg. gold with 350 to 420 mg. silver remain unbroken under this treatment; those with larger proportions of silver break up. For average ores, he recommends 20 per cent by volume, and a second (50 per cent) acid only when the beads are large. E. A. Smith advises boiling large buttons with a second acid of sp. gr. 1.30.

T. K. Rose recommends acid of sp. gr. 1.10 for flattened beads containing a large proportion of silver but considers 1.20 (equal volumes) satisfactory for all cases if the silver ratio is not over 4 or 5:1. He insists on the advantage, often overlooked, of using rather hot acid at the start, which, to a great extent, avoids breaking up and leaves the gold compact and yellow in color.

In general, the smallest amounts of gold require the largest silver ratios; this principle has been vaguely followed, but Rose has specified some fairly definite ratios:

Milligrams gold	Ratio Ag to Au about	Weight silver required, milligrams
Under 0.1	20 or 30	2 to 3
0.2	10	2
1	6	6
10	4	40
Over 50	2.25	112 and up

The last ratio, 2.25, is decidedly lower than commonly used; most assayers would probably use 4, or 5:1, even with rich ores, although 2.5 or 3 would be preferable. Large buttons, leaving coherent masses of gold, should always be boiled with a second fairly strong acid and thoroughly washed.

For diluting the acid used in parting, it is desirable to use distilled water quite free from chlorine, but rain water may generally be substituted with safety, if carefully collected. In some few districts the waters of rivers and lakes contain only about one part chlorine per million and give no appreciable precipitate of silver chloride; such water can be safely used for diluting and washing.

In case the only water available contains chlorides, it may be treated with sufficient silver nitrate (after faintly acidifying with nitric acid) to insure precipitation of all the chlorine as $AgCl$; this, after thorough agitation, is allowed to settle for several hours, and the clear liquid decanted or siphoned off. If the nitric acid is itself contaminated with HCl or chlorides, it may be similarly precipitated after dilution. In parting large buttons, as in the assay of bullion or precipitate, the dissolved silver reacts at once with any chloride ion present and appears to prevent appreciable action on the gold, even when enough chlorine is present to yield a visible precipitate of silver chloride; this precipitate is, however, objectionable and may itself introduce an error by contaminating the spongy gold. If such a precipitate is unavoidable, it should be removed by treatment with dilute ammonia and washing with water before annealing, but after the parting acid has been decanted off and the gold washed nearly free from acid.

Inquartation

As previously stated, inquartation signifies the addition of silver to an alloy of gold silver in sufficient amount to permit of the complete solution of the silver by acid leaving the gold in pure but coherent form. Formerly, the ratio Ag to Au = 3:1 was considered necessary; hence, the term *inquartation.* The best method of inquarting is to wrap pure silver foil with the bead or button in sheet lead, usually 2 to 5 g., and cupel in a preheated cupel.

Beads which need inquartation may also be fused with silver, on a piece of charcoal, by means of the blowpipe; but this method is not to be recommended, as it frequently occasions loss.

Many assayers, if they suspect an ore to be deficient in silver for parting, add silver to the crucible, not determining the silver in this assay but running a separate scorification assay for this purpose.

Another way[1] is to add to the charge a desired number of cubic centimeters of $AgNO_3$ solution of such strength that 1 cc. contains 1 mg. Ag. The proper deduction can then be made from the weight of the bead, but some allowance must be made for the silver absorbed by the cupel.

[1] Hawley, F. G., *Eng. Mining Jour.*, vol. XC, p. 649.

CHAPTER X

THE ASSAY OF ORES AND METALLURGIC PRODUCTS CONTAINING IMPURITIES

Impurities, from the assayer's point of view, are such substances, contained in ores, furnace products, or other material, as necessitate some particular method of assay or treatment or the observance of special precautions not included in the ordinary crucible assay as already outlined.

Common impurities are sulphur, arsenic, tellurium, antimony, zinc, copper, etc. Of these sulphur is by far the most common.

In performing an assay it is usually the aim of the assayer, whenever this is possible, to produce by direct fusion, either by the crucible or by the scorification method, a pure lead button weighing approximately 20 g. If the button is smaller than this, there is danger of not collecting the values; if larger, cupellation is too prolonged and losses are increased. In the assay of low-grade gold ores it may be desirable to produce lead buttons of 25 to 30 g. in order to obtain the best results. The impurities mentioned affect either the size of the button or the purity of the button, or both. To show the effect of sulphur, the following definite example is taken:

Given an ore containing pyrite, which, in a charge yielding the ordinary type of monosilicate slag, gives a reducing power of 5 g. of lead per gram of ore. If the following charge:

15 g. ore	70 g. PbO
30 g. Na_2CO_3	8 g. SiO_2

Borax glass cover

be made up and fused, a 60-g. button (approximately) will be produced, on top of which will be a small quantity of "matte," *i.e.*, an artificial sulphide of the metals, in this case iron and lead. This matte is brittle and may contain some silver and a little gold. On hammering the lead button the matte crumbles and is lost. In general, it is an undesirable product to make. A small amount of matte is produced in this case, since the ore has the

power to reduce 75 g. of lead from PbO, while only 70 g. of PbO are present, so that the excess sulphide of the ore not acted upon by the PbO remains in the charge, uniting with some of the lead to form a sulphide of iron and lead. The button is also much too large to cupel. If in the charge the PbO is materially increased, the ore will react to the extent of its full reducing power, a lead button of 75 g. will be produced, no matte will be found, and the slag will be improved, owing to the addition to it of the fusible base PbO. If the PbO in the charge be materially reduced, the lead button will be much smaller (owing to the dearth of PbO available for reduction), considerable matte will be formed, and the slag will be poor.

If the silica be increased, so that sufficient be present to form the higher silicates with all the bases present, practically no lead will be reduced, for the sulphide has not the power to reduce much Pb from lead-soda silicates unless a free base be present, *e.g.*,

$$(PbO.Na_2O)2SiO_2 + FeS_2 \text{ (no action)},$$

or, possibly,

$$(PbO.Na_2O)2SiO_2 + FeS_2 = (FeO.Na_2O)2SiO_2 + PbS + S$$

In this way, the sulphur remains in the charge in the form of sulphide sulphur.

Soda will cause the formation of SO_3, if PbO is present to furnish the oxygen, and if it can act as a free base, *i.e.*, if it is not combined with silica (see Chap. VI, on Reduction and Oxidation Reactions). An increase of soda without an increase of PbO or SiO_2 will lessen the amount of matte, as sulphur will tend to combine, to some extent, with the Na_2O to form, with the FeS, a double sulphide of iron and soda, etc., which will be dissolved in the slag. The above outlines the effect of such impurities as sulphur and arsenic and shows the necessity of special methods of assay directed toward the getting rid of impurities.

The impurities mentioned may be divided into two classes:

a. Those which can be volatilized by oxidation or otherwise, *e.g.*, sulphur, arsenic, and antimony.

b. Those which cannot be volatilized, *e.g.*, copper, zinc, etc. Some of these may be partly volatilized, as antimony and zinc. For the removal of all of them, however, whether by volatilization or by slagging, oxidation is essential.

In one method employed on light sulphide or arsenic ores, the iron-nail method, sulphur and arsenic are carried into the slag as a double sulphide or arsenide of soda and iron, etc.

The following methods are standard ones for the assay of impure ores and are discussed in detail:

Crucible fusions.....
1. The roasting method.
2. The niter method.
   a. The common niter method.
   b. Miller's oxide-slag method.
   c. Perkins' excess-litharge method.
3. The iron-nail method.
   a. The niter-iron method.
4. The cyanide method (rarely used).

5. The scorification method.
6. The combination wet-and-dry method (removal of impurities by solution).

The Roasting Method.—It is usual to weigh out accurately 0.5 or 1 assay ton of the ore to be assayed and place it in a roasting dish of sufficient size to permit of stirring without loss by spilling. The dish is placed in the muffle the temperature of which is not above a "black red" and the firing of which is under good control, so that the temperature will not rise too rapidly. In the case of an ordinary sulphide ore, such as a pyrite, or, for example, a chalcopyrite and quartz, the following reactions take place, if the roasting is carried on slowly at a low heat:[1]

$$3CuFeS_2 + 18O + \text{heat} = Cu_2S + 3FeSO_4 + CuSO_4 + SO_2$$

At 590° C., the ferrous sulphate decomposes spontaneously, sulphatizing the balance of the copper:

$$Cu_2S + 2FeSO_4 + 6O = 2CuSO_4 + Fe_2O_3 + SO_3$$

At 655° C., the copper sulphate decomposes into basic sulphate and SO_3, and at 700° C. into CuO and SO_3, as follows:

$$2CuSO_4 = CuO.CuSO_4 + SO_3$$
$$CuO.CuSO_4 = 2CuO + SO_3$$

so that the final products of the roast, when carried to above 700° C., are ferric and cupric oxide, with a complete removal of the sulphur. If the temperature is not carried above 700° C.,

[1] Bradford, R. H., *Trans.* A. I. M. E., vol XXXIII, p. 68.

sulphur remains in the charge as sulphate, which again may be reduced in the crucible to sulphides:

$$2CuSO_4 + 3C = Cu_2S + SO_2 + 3CO_2$$

If, for any reason, it is not desirable to carry the temperature so high as 700° C., the ore, after roasting until no further smell of SO_2 is discernible, may be cooled and mixed with 5 to 10 g. of powdered ammonium carbonate and reroasted at a low heat, the sulphuric anhydride (SO_3) being eliminated as volatile ammonium sulphate, $(NH_4)_2SO_4$:

$$CuSO_4 + (NH_4)_2CO_3 = CuO + (NH_4)_2SO_4 + CO_2$$

Any silver in the ore that has been roasted will be in the form of Ag_2SO_4 or, if arsenic and antimony are present, partly in the form of arseniates and antimoniates. If the roasting temperature is carried to 870° C. and above, the silver sulphate will be decomposed, leaving the silver in the form of metallic silver. In order to avoid loss of silver, it is best not to carry the temperature above 700° C.

In roasting simple pyrite ores, the reactions are similar but simpler, and the temperature need not be carried above 600° C. During roasting, the ore should be stirred frequently in order to expose fresh surfaces to oxidation.

When ores contain arsenic and antimony, the roasting operation is more difficult and complex, and considerable care and skill are required to eliminate the greater part of these two volatile elements. The reason for this is that the arsenic and antimony pass by roasting first to the state of the lower oxides As_2O_3, Sb_2O_3, which are volatile, and then to the state of the higher oxides As_2O_5, Sb_2O_5, forming arseniates and antimoniates of certain metals present in the ore, some of which are stable even at high temperatures, thus fixing the arsenic and antimony in the roasted ore and not eliminating it. The arseniates (or antimoniates) which ordinarily form are those of copper, iron, and silver. The best conditions for the elimination of arsenic and antimony are alternate oxidation and reduction at a low heat. The presence of sulphur tends to aid the elimination of arsenic and antimony by the formation of the volatile sulphides of these elements. The reducing action necessary for the elimination of arsenic and antimony is best obtained by mixing with the ore equal volumes of coal dust or charcoal and roasting at a dark-red

heat until the coal is burnt off, then cooling, adding more coal dust, and reroasting. In this way, the greater part of the arsenic and antimony can be readily volatilized, except in very rich silver ores. When galena ores are to be roasted, the ore is best mixed with an equal volume of silica and roasted at a very low heat In this roast, $PbSO_4$ is formed to a considerable extent, which at a higher heat is decomposed by the SiO_2 present, as follows:

$$PbSO_4 + SiO_2 = PbSiO_3 + SO_3$$

Care must be taken with this roast as, at the formation point of lead silicate, silver losses are apt to occur. A successful roast will be indicated by a yellow color (lead silicate), and an unsuccessful one by a black or gray color (fused, undecomposed sulphides). In general, heavy sulphide ores that contain their chief value in gold may be roasted, when this is carefully done, without loss of gold; but silver ores, especially when of high grade, are apt to give low results.

In making up the charge for the roasted ore, it is to be noted that from a sulphide ore (pyrite, etc.) the product is frequently of an oxidizing nature and basic, which must be taken into account in adding the fluxes. In galena ores, when silica has been added, this must be accounted for.

The roasting method is used only for heavy sulphide ores, especially when they have a low value in gold and silver, as it permits of a large amount of ore being taken (1 assay ton and more), which after roasting presents no difficulty in making the proper fusion. The great disadvantage of roasting lies in the considerable time and personal attention required for a careful roast. If not carefully performed, an appreciable mechanical loss may result, as is evident from the sparks produced by decrepitating particles. Modern assayers seldom use the roasting methods.

The Niter Method.—The first step in the niter method is the making of a preliminary assay according to the directions already given. The precautions concerning the reducing power of the sulphides in different types of charges must be carefully noted; it is best to have the preliminary charge of the same composition as the final assay charge; or else the reducing power may be determined by the soda-litharge charge and this cut down by 25 per cent, 20 g. deducted for the lead button, and the remainder

divided by 4 to get the number of grams of niter to be added, if the monosilicate slag is to be made in the assay.

The amount of ore taken for the niter assay varies according to the grade of the ore in gold and silver and according to the amount of impurity present. It is rarely desirable to add more than 20 g. of niter to the charge, as larger amounts cause difficulty through the evolution of too much gas. The amount of ore most frequently taken is 0.5 assay ton. Sometimes, with ores containing much impurity, 0.10 to 0.25 assay ton is used. For amounts of 0.5 assay ton of ore and less, 20-g. crucibles (170 cc. capacity) are used, and 30-g. crucibles (240 cc. capacity) for 1 assay ton of ore.

Miller's Oxide-slag Method.—This method is a modified niter method applicable to such ores as contain practically no silica, *i.e.*, heavy sulphide ores, such as pyrites, arsenopyrite, mattes, etc. It is based on the fact that PbO has the power to hold in solution and in suspension oxides of such metals as copper, iron, etc. (see scorification), in certain amounts. Niter is added to oxidize the sulphides, etc., and Na_2CO_3 to aid in the complete oxidation of the sulphur by the formation of sulphates, in the manner already discussed. The first step, as in the ordinary niter method, is the preliminary assay, according to the following charge:

	Grams
Ore	3
PbO	50
Na_2CO_3	8

The final charge is as follows:

Ore	0.5 a. t.
PbO	70.0 g.
Na_2CO_3	12.0 g.
KNO_3	(calculated for a 20-g. button)

Quick fires, 1100° C., 30 min., are found to be best. The slags are usually dull black and pour readily, and the button separates easily from the slag. (In slags high in silica or containing much borax, the lead buttons are apt to adhere closely to the slag.) With the oxide-slag method, trouble is sometimes experienced through the lead's refusing to collect and remaining shotted through the slag. The difficulty is usually due to too much soda (especially if considerable niter is used), although a too low temperature of fusion is also a factor.

The method gives reliable results on gold and silver, comparing well with the other standard methods.[1]

Perkins' Excess-litharge Method.[2]—This method is based on the fact that PbO will dissolve oxides of other metals and, if present in great excess, will prevent, to a large extent, the reduction of other metals, such as Cu and Sb. The presence of so much PbO also insures a strongly oxidizing tendency in the crucible, preventing impurities from entering into the button.

It is desirable to add or have present SiO_2 in such an amount as will form a monosilicate with the bases present, including some litharge, but leaving much litharge uncombined in the charge.

The following table shows the proportion of PbO required to form fusible compounds with the principal metallic oxides:[3]

TABLE XXVII.—PbO REQUIRED WITH METALLIC OXIDES

One part of....	Cu_2O	CuO	ZnO	Fe_3O_4	Fe_2O_3	MnO	SnO_2	Sb_2O_3	As_2O_5
Requires parts of PbO......	1.5	1.8	8	4	10	10	13	5	1

In order to carry out the excess-litharge method intelligently, it is necessary to know the approximate composition of the ore, so as to provide the proper amount of PbO and SiO_2. The best fusion exhibits, in a section of the cone of the slag after breaking, silicates of lead, iron, etc., on the outer surface, gradually passing to crystalline litharge toward the center. The temperature of fusion should not exceed 1050° to 1100° C. It must be above 884° C. (melting point of PbO). The first step is the making of a preliminary assay in order to determine the amount of niter to be added.[4]

The final charge most frequently used is:

Ore........	0.25 to 0.5 a. t.	Na_2CO_3....................	12 g.
PbO.......	8 to 10 a. t.	SiO_2......................	10 g.

Niter to obtain 20-g. button

The button is generally clean and separates easily from the slag.

[1] MILLER, HALL, and FALK, "The Reduction of Lead from Litharge," etc., *Trans.* A. I. M. E., vol. XXXIV, pp. 398, 399.

[2] PERKINS, W. G., "The Litharge Process," *ibid.*, vol. XXXI, p. 913.

[3] HOFMAN, H. O. "Metallurgy of Lead," p. 7, 1904.

[4] In place of niter, it may be necessary, in this or in Miller's method, to add argol, if ore is not reducing.

The excess-litharge method will give somewhat low results on silver, especially on high-grade ores, but will give good results on gold. In ores of the following analysis: SiO_2 40 to 60 per cent; Fe, 5 per cent; CaO, 2 per cent; Pb, 15 to 40 per cent; Zn, 2 per cent; Ag, 20 to 80 oz.; S, 1 per cent; and a trace of copper, the results in the accompanying table were obtained by the use of charges A, B, and C.[1]

	Charge A	Charge B	Charge C
PbO	25 g.	50 g.	75 g.
Borax glass	4 g.	4 g.	4 g.
Flour	2.25 g.	2.25 g.	2.25 g.
Na_2CO_3	16.0 g.	16.0 g.	16.0 g.
K_2CO_3	25.0 g.	25.0 g.	25.0 g.
Ore	0.5 a. t.	0.5 a. t.	0.5 a. t.

TABLE XXVIII.—AVERAGE FIGURES SHOWING EFFECT OF AN INCREASE IN PbO ON SILVER RESULTS[2]

Ore number	Ounces silver found per ton		
	Charge A	Charge B	Charge C
1	51.05	50.86	50.62
2	42.36	42.20	42.02
3	27.82	27.70	27.55

An ore from Cobalt, Can.,[3] containing 5.06 per cent Ni and 9.12 Co, chiefly as niccolite and smaltite, and some free silver was assayed by the following charge:

Ore	0.05 a. t.
$NaHCO_3$	10 g.
Borax glass	10 g.
Argol	1.5 g.
Litharge	as given in table

[1] WILLIAMS, KENNETH, *Jour. Ind. Eng. Chem.*, vol. II, p. 406.

[2] See also: The Solubility of Ag_2O in PbO, Kohlmeyer, E. J. *Chem. Zeit.*, vol. XXXVI, p. 1079–82 (1912) and *Chem. Abstracts* Vol. VII, p. 457 (1913).

[3] LODGE, R. W., "The Effect of High Litharge in the Crucible Assay for Silver," *Trans.* A. I. M. E., vol. XXXVIII, p. 638.

TABLE XXIX.—AVERAGE FIGURES SHOWING THE EFFECT OF AN INCREASED AMOUNT OF PbO ON SILVER RESULTS

Litharge, grams	Lead button, grams	Silver, ounces per ton	Silver in slag, ounces per ton	Silver in cupel, ounces per ton
30	19	2,051.4	9.6	34.0
40	21	2,056.0		
40	21	2,050.0		
80	30	1,968.6		
80	22	1,944.6	135.2	35.0
80	21	1,984.8	70.2	34.6
80	21	1,914.8		

The Iron-nail Method.—This method does not attempt to oxidize impurities but aims to carry sulphur, etc., into the slag. The ore is decomposed by the iron nails added to the charge and by the PbO present. As iron reduces PbO to Pb, the amount of litharge added to the charge is limited to 25 to 30 g. The amount of soda needed is large, as this flux is depended upon to carry the sulphur into the slag. The slag should be below a monosilicate in degree and high in soda, as basic alkaline slags have a high solvent power for sulphides.

A typical charge on an ore that has a reducing power of about 4 g. of Pb per gram of ore is:[1]

Ore	0.5 a. t.	SiO_2	2 g.
Na_2CO_3	20 g.	borax glass	8 g.
PbO	30 g.	nails	17 g.

Salt cover

The soda should usually be twice the amount of ore in the charge. The reactions that take place are approximately as follows:

$$7PbO + FeS_2 + 2Na_2CO_3 = 7Pb + 2Na_2SO_4 + FeO + 2CO_2$$

Part of the ore is decomposed by the PbO, and part of the S may go off as SO_2, as discussed in previous pages. The iron nails decompose the balance of the sulphides:

$$FeS_2 + Fe = 2FeS$$

$PbS + Fe = Pb + FeS$ (if galena is present or lead sulphide forms).

[1] LODGE, R. W. "Notes on Assaying," p. 99.
HALL, W. E. and DRURY, C. W., *Trans.* A. I. M. E. vol. XLVII, p. 32.

The iron sulphide (FeS) is dissolved by the alkaline slag, forming, probably, double sulphides of soda and iron.

To show the nature of the iron-nail fusion, the following results of two fusions on a pyrite ore containing 39.5 per cent S—a reducing power equal to about 8—are given.[1] In these experiments, sodium bicarbonate was used instead of soda ash.

	Charge 1	Charge 2
Ore	1 a. t.	0.5 a. t.
$NaHCO_3$	30 g.	30 g.
PbO	30 g.	30 g.
SiO_2	4 g.	4 g.
Nails	4	4
Borax glass cover	10 g.	10 g.

The following results were obtained:

	No. 1, grams	No. 2, grams
Slag	60	65
Matte	23.5	None
Lead	24.5	26.5
Crucible and charge before fusion	685	662
Crucible and charge after fusion	665	642
Loss in weight[1]	20	20
Nails before fusion	64	63
Nails after fusion	43	49
Loss of iron	21	14
Per cent of S in slag	6.73	7.63
S in slag	4.03	4.96
S in ore	11.85	5.92
S passed off as SO_2	0.95	0.96
S in matte	6.87	None

[1] This is due to expulsion of approximately 3 g. H_2O, 16 g. CO_2, and 1 g. S.

It will be noted that the charges are identical as far as the fluxes are concerned but that the amount of ore differs. It is desirable in heavy sulphide ores to keep the ore down to 0.5 assay ton and lower if necessary.

Care must be taken not to have the slag above a monosilicate in degree, for if higher in SiO_2 there will be particular danger in

[1] *Ibid.*, p. 101.

this charge of not having the sulphides oxidized by the PbO, more sulphide being retained in the charge than it can dissolve, and forming a matte, even with a small amount of ore.

The Niter-iron Method.—This method is, in principle, the same as the iron-nail method. An amount of niter is added at random, sufficient to oxidize but a portion of the sulphides, the balance being decomposed by the nails.

The Cyanide Method.—Sometimes, when no other fluxes are at hand, or when a rapid assay is to be made in which accuracy is not essential, a fusion of ore with cyanide may be made, and the resultant button cupelled for silver and gold. The method is a rapid one and gives good malleable buttons but is apt to be low in gold and silver, especially in silver. The cyanide used should be pure, free from carbonates or other impurities, and the fusion should be made at a low temperature. The following charge is used:

Ore	0.5 to 1 a. t.
PbO	25 g.
KCN	3 a. t.

When the ore contains copper and other base-metal impurities, these are reduced and enter the lead button. Sulphur is taken up by the slag as potassium sulphocyanate (KCNS). In general, it is a method not to be recommended. The following results show the loss in silver which takes place in this method:[1]

Table XXX.—Loss of Silver in Cyanide Method

	Niter method, milligrams	Cyanide method, milligrams
Silver, by uncorrected assay	563.73	525.5
Silver in slag	4.10	36.8
Silver from cupel	7.81	6.56

The results are averages of duplicate assays. The loss of gold in the slag by cyanide fusion is not nearly so marked as that of silver.

A Comparison of the Different Crucible Methods of Assay for Impure Ores.—In very impure ores, containing large amounts of

[1] Miller, E. H., "Corrected Assays," *School Mines Quart.*, vol. XIX, p. 43, 1897.

sulphur, arsenic, etc., the roasting method is applicable when gold only is to be determined or when silver results need not be very accurate. This method gives uniformly lower silver results than most of the other methods, although, to a large extent, this is due to roasting at a too high temperature. The roasting method has the advantage that when ores are low grade, large quantities of ore can be taken, which is not always possible with the other methods. Roasting, however, must be skilfully conducted in order to be successful.

The niter method is a desirable and clean method of assay giving accurate results. Where large quantities of niter are employed, the oxidizing action in the crucible is greatly increased, and it is probable that thereby losses in silver are apt to occur by the slagging of the silver.

There is no positive accumulated evidence on this subject, but many assayers hold this opinion.[1] The niter method is desirable for such ores as do not contain sulphur enough to require extraordinary amounts of niter. Usually, the limit of niter in a charge is placed at about 20 g.; if the ore should require more than this, it is generally considered advisable to reduce the quantity of ore taken for the assay. This has the disadvantage of multiplying the error of the assay, when finding the value per ton. Some assayers, however, use 40 g. or even more.

The modified niter methods discussed offer advantages in the slagging of base-metal impurities. This is particularly true of copper and zinc. It is very much easier to cause copper to enter the slag when an oxide slag is made than when a silicate is. This is partly due to the oxidizing nature of the high litharge charges. The best method for the slagging of copper or other base-metal impurities is the excess-litharge method.

The iron-nail method is a standard one, which can be successfully applied to most sulphide ores and, with care, to arsenical ones. It is not applicable to ores containing base-metal impurities, such as copper, for, being essentially reducing in its nature, practically all of the base-metal impurities will be found in the lead button. When used with arsenical ores, the temperature

[1] Woodward, E. C., *Mining Sci. Press*, vol. CII, p. 301, gives data which rather tend to show that niter does not have this effect. In 85 samples of an average value of 167 oz. per ton, scorification (0.1 a. t.) gave results averaging 0.918 oz. (0.55 per cent) more than the crucible method (0.5 a. t.) with niter varying from 6 to 25 g. These were umpire determinations, each averaged from six fusions.

employed should be low, not above 1050° C.; otherwise, speiss (an artificial arsenide of iron) is apt to form, which may carry values. It also has the objection, in the case of very impure ores, that small quantities must be taken for assay, involving serious risk of multiplying an error of assay.

Scorification.—This is the oxidizing fusion of ore with metallic lead in the muffle furnace, producing, in the main, a litharge slag, *i.e.*, an oxide slag. It is a method of assay which requires no previous preparation of the ore or a preliminary assay, and as practically only one flux is employed, it is both a cheap and a rapid method. It is also a thoroughly reliable method, when proper precautions are taken and when it is employed on material suitable for the purpose. The operation is performed in shallow fire-clay dishes, called *scorifiers.*

The sizes commonly used are

Size of Scorifiers Inches	Volume Cu. Cm.
1.5	15
2.0	25
2.5	37
3.5	100

The dimensions referred to are outside diameters. The size most commonly employed is the 2.5-in. one. Before these dishes are used, some assayers line them with ferric oxide. This is done by preparing crushed iron ore or ochre, by mixing with water, and by painting the inside of the dishes, or by rubbing the surface with a lump of ochre or with a soft red crayon. This gives them a basic lining and, to some extent, prevents the oxide slag from attacking the silica in the clay.

Some scorifier slags, especially if they contain copper, are very corrosive. The amount of ore taken for scorification varies from 0.10 to 0.25 assay ton; but 0.10 assay ton is the amount most frequently taken. The larger amounts are rarely used, unless the ore contains practically no bases. Sometimes, as little as 0.05 assay ton is taken if the material is very impure or extremely rich in gold or silver, as is the case of some electrolytic slime or precipitate from cyanide or "hyposulphite" leaching processes. The amount of test lead varies according to the nature of the ore. The more impure the ore the larger will be the ratio of lead to ore. With 0.10 assay ton, the test lead will vary from 40 to 100 g. A common charge is 40 to 50 g. of test

lead for ordinary ores. As already pointed out, certain quantities of litharge are required in order to make fusible compounds with the metallic oxides. If the ore contains small amounts of the metallic oxide, the test lead will be small in amount; if it contains appreciable quantities of ferric oxide (Fe_2O_3) or Cu, etc., large amounts of test lead will be required. It is best to add a small amount of borax glass to the charge, from 1 to 1.5 g., scattering it over the surface of the lead. This aids in the solution of the bases present. When the ore contains the basic oxides mentioned, borax glass up to 3 and 4 g. will materially aid in forming good slags, without infusible scoria. This infusible scoria often appears in ores containing large amounts of bases and is very apt to give low results by entangling unfused portions of ore within itself. It is best to mix the weighed-out portion of ore with one-half of the test lead to be used and then cover over with the balance.

The scorification may be divided into the following distinct steps:

1. *Melting.*—In this stage, the lead melts, and the ore, being of a lesser gravity, rises to the surface of the molten lead and floats there.

2. *Roasting.*—The ore on the surface of the lead is attacked by the oxygen of the air and roasts in the same way as described under Roasting of Ores.

3. *Scorification Proper.*—The lead commences to oxidize, forming litharge. A small percentage (3) volatilizes and the balance forms a fusible slag. This now absorbs the oxides formed by the roasting, dissolving them and forming an igneous solution. The silver and gold, liberated, are absorbed by the remaining metallic lead. The slag, as it forms, drops to the side, forming a slag ring, with the center of the lead bath open to the atmosphere. The reason for this is that the meniscus of molten lead is convex, thus causing the collecting of the slag on the rim of the scorifier. The scorification continues until the whole of the lead is covered over with slag. It is then considered finished and the assay is poured. Should the assay be left in the muffle, the lead will still continue to oxidize, although none is exposed to the air, the interchange of oxygen taking place by means of the litharge and other oxides present. The size of the lead button desired from this assay ranges from 15 to 20 g. If the scorification is continued to produce smaller

buttons, losses are apt to occur by oxidation of the silver, especially if this is present in considerable amounts, thus forming rich slags.

The temperature of scorification ranges from 1000° to 1100° C., although with pure ores higher temperatures may be employed.

When impure ores containing much base metal are scorified, the buttons from the scorification are very apt to be contaminated with base metal, especially copper, and will then have to be rescorified with more test lead, in order to get a pure button for cupellation. Hard buttons are always impure.

All metals are, to some extent, oxidized simultaneously, but a mixture of metals may be roughly separated by successive oxidation, each metal, in turn, partially protecting the metal next in order, while the latter may act as an oxygen carrier to the former.[1] The order of oxidation is as follows:

Fe to Fe_2O_3	Cu to Cu_2O
Zn to ZnO	Pt to—
Pb to PbO	Ag to Ag_2O
Ni to Ni_2O_3	Au to AuO

The order of oxidation of the following elements is not so certain:

Sb to Sb_2O_3	Bi to Bi_2O_3
As to As_2O_3	Te to TeO_2
C to CO_2	S to SO_2

The order given in the table shows the difficulty encountered in the removal of copper by scorification, as lead stands ahead of it in the order of removal, and it is very difficult and requires a number of rescorifications, if the amount of copper is large, to reduce it to such an amount as to prevent loss in cupellation. Iron and zinc are very readily removed by scorification (oxidation), part of the zinc being volatilized. Certain elements, like Te and Se, are difficult to remove from the lead button and may tend to concentrate with the Au and Ag in the final cupellation.

The slag from the scorification assay should be homogeneous and glassy. If it has an earthy appearance, it is an indication of a too low temperature's having been used, and the button is apt to be brittle, due to contained PbO. White patches of

[1] Rose, T. K., "Refining Gold Bullion, etc., with Oxygen Gas," *Trans. I. M. M.*, vol. XIV, p. 377, 1905.

sulphate of lead on the slag after pouring also indicate a rather too low temperature of scorification, as this sulphate forms at a low temperature under slow oxidation.

The scorification method is a reliable one on most materials, with the exceptions enumerated below. As the usual quantity taken for assay is 0.1 to 0.2 assay ton, it is evidently not a suitable method for low-grade ores, especially low-grade gold ores, where at least 0.5 to 1.0 assay ton must be taken in order to get accurate results and avoid the multiplication of the error of weighing. It is practically impossible to get reliable results on $5 to $10 gold ores by ordinary scorification. If, however, 10 assays of 0.1 assay ton are made, the buttons from these combined and rescorified into one button, which is then cupelled, the results are reliable but not so good as from the crucible assay on the same total amount, on account of the multiplicity of weighing and other operations, which occasion errors and losses. The method, in this instance, would also be more costly of time and materials.

For ordinary and rich silver ores, and very rich gold ores or furnace products, such as bullions, mattes, etc., the method is a desirable one. It requires no preliminary operations and thus saves valuable time. The slag loss is frequently somewhat higher than in the crucible assay. It is, as ordinarily performed (in duplicate), a cheap method as regards fluxes, etc. It does not give good results on very basic ores, *i.e.*, those containing hematite, manganese oxides, etc., as in this case, unless a great deal of lead is used, scoria are apt to form in the slag, which may entangle lead and undecomposed ore. Neither does it give good results on telluride ores, cyanide precipitates, or ores that contain chloride of silver.

When basic material is to be scorified, small additions of SiO_2, up to 1 g., may prove advantageous. In general, however, the addition of fluxes, except test lead, is not to be recommended. Scorification may be modified by the addition of considerable amounts of borax glass, litharge and silica, when it approaches the crucible assay in character with none of its advantages.

The Combination Method.—The trouble arising from the presence of considerable amounts of base metals, such as copper and zinc, has been fully discussed in previous pages, as well as the difficulty of their removal by fusion methods. For this reason, the combination wet- and dry-method has been developed, to remove the objectionable impurities by solution. The method

is used chiefly on copper-bearing material, such as heavy copper ores, copper mattes, blister copper, and, to a lesser extent, on zinc ores, and on cyanide precipitates produced by zinc, and has been advocated for telluride ores.

Van Liew's Method for Blister Copper.—This is a standard method for copper material. Weigh out duplicate samples of 1 assay ton each of copper borings, add 350 cc. cold water and 100 cc. HNO_3 (sp. gr. 1.42), and set in a cool place for 20 hours, stirring from time to time. Then, if the copper is not dissolved, add from 5 to 30 cc. more of concentrated acid. At the end of 26 to 28 hours, the solution of the copper is complete. Do not apply heat, in order to minimize the solution of small quantities of gold by whatever action this may take place. The oxides of nitrogen in the solution are removed by blowing air into it for 20 to 30 min.

Salt solution (containing 0.542 g. of NaCl per 1,000 cc.) is added in sufficient quantity to precipitate the Ag present as chloride.[1] One cubic centimeter of this solution will precipitate 1 mg. of Ag, and an excess of 4 to 8 cc. above that required for the Ag should be added. If the amount of Ag in the copper is small, add 10 cc. of a saturated solution of lead acetate and 2 cc. of concentrated H_2SO_4 in order to form $PbSO_4$, to aid in settling the silver chloride. Let this stand for about 12 hours, filter the precipitate into the proper-sized filter, and wash it well into the point of the filter paper. Dry the filter carefully in the air bath and, when dry, add 8 g. of test lead on top of the precipitate, and carefully transfer to a scorifier containing 2 g. of lead. This is placed in the muffle, heated just to incipient redness, and the filter papers burnt off, but only until the flame disappears and not into ash. This takes only a minute or so, the precaution being taken to prevent loss of silver by volatilization as AgCl, the lead and carbon present reducing the AgCl to Ag. Then add 3 to 4 g. of PbO, and the same amount of borax glass, raise the heat until well molten, and pour. No scorification is necessary, as no impurities are present. The lead button will weigh 5 to 8 g. and is cupelled with feather litharge. The results should check within 0.2 to 0.3 oz. for Ag and very closely for gold.[2]

[1] It must not be forgotten that the addition of sodium chloride to a nitric-acid solution produces aqua regia, however small the amount.

[2] Van Liew, R. W., in *Eng. Mining Jour.*, vol. LXIX, p. 498 *et seq.*

Sulphuric-acid Method for Blister Copper.[1]—To 80 cc. of concentrated H_2SO_4 add 25 cc. of a solution of $CuSO_4$ (160 g. per 1,000 cc.), using a low, wide No. 5 beaker. Heat to such a temperature that on the addition of the copper borings action commences immediately; add 1 a. t. borings, spreading them over the bottom of the beaker. Heat until all dissolving action has ceased, usually from 1 to 1½ hours; then cool and add 400 cc. of distilled water, stirring to prevent caking of the crystals. Bring to just a boil, filter, and wash the beaker thoroughly, using a rubber-tipped glass rod as a stirrer. Place the filter paper with the residue in a 2.5-in. scorifier, dry and burn off the paper; add 35 g. test lead and 1 g. silica, scorify to a button of about 9 g., cupel, and part as usual.

Silver may be determined by adding salt solution, as in Van Liew's method, and 10 cc. of a 10 per cent solution of lead acetate, stirring well and letting stand overnight. Then filter with the usual precaution, add the paper and precipitate to the same scorifier containing the gold, and proceed as in the case of gold only.

In place of cupric sulphate, mercuric nitrate or mercuric sulphate[2] may be used, the equivalent of about 100 mg. of mercury for an assay ton of borings. The mercury salt is best added to the copper borings, stirring a little and then adding the 80 cc. sulphuric acid and boiling on a hot plate for ¾ hour. Then proceed as already described. When mercury salt is used in the above quantity on low-grade bullions containing from 10 to 50 oz. Ag per ton, all the silver is thrown down with the gold. If more silver is present, salt solution should be added in sufficient quantity to precipitate the silver and any mercury that has passed into solution.

The object of the addition of cupric sulphate or the mercuric salt is to prevent the formation of copper sulphides, which will remain in the residue and make necessary more than one scorification to remove the copper before cupellation.

The sulphuric-acid method is stated to give results equal to the "all-fire" method on gold.

Gold and Silver in Copper Bullion.—The following method was adopted by Dr. Edward Keller for use with the blister and

[1] Hunt, F. F., "Determination of Gold in Copper Bullion," *Eng. Mining Jour.*, vol. LXXXVII, p. 465.

[2] Flinn. F. B. *Eng. Mining Jour.*, vol. LXXXVII, p. 569; also *Mining Sci. Press*, vol. CI, p. 148.

refined copper from the Anaconda mines, in which the determination of silver and gold is most important. His paper,[1] read at Butte in 1913, discusses the shortcomings of other methods and the evolution of the sulphate-mercury method of dissolving copper, by which even coarse drillings and shot can be completely sulphatized and both gold and silver accurately determined in one sample. The elaborate mechanical contrivances, used by Dr. Keller for carrying out a number of parallel determinations at once, are described fully in other papers.[2]

Stock solutions required: mercuric nitrate, 25 g. Hg per liter.

Sulphuric acid, sp. gr. 1.84.

Sodium chloride, 19 g. NaCl per liter (1 cc. precipitates 35 mg. silver).

The copper-bullion drilling sample is ground in a steel mill to pass a 16-mesh screen. If the coarse and fine parts, as separated by a 40-mesh sieve, probably differ in precious-metal content they are weighed separately in their proper ratio to make 1 a. t. Thus, if C = weight of coarse and F = weight of fine in the total sample, the number of grams of fine to be first weighed out is

$$\frac{29.166}{\frac{C}{F} + 1}$$

and the remainder of the assay ton is made up of coarse. This is now placed in an 800-cc. pyrex beaker, and 30 cc. water and 10 cc. of the mercuric nitrate solution are added. The beaker is shaken until the copper is all amalgamated, and 100 cc. sulphuric acid are added, the beaker is covered with a watch glass and placed on an electric hot plate. The time required for solution varies, but it is usually complete in about 2 hours. For about an hour, the acid appears to boil, owing to evolution of sulphur dioxide. The liquid then becomes dark green, finally changing to light grayish blue. The beaker is removed to an asbestos sheet to cool somewhat, as the temperature may rise to over 200° C. or 400° F. Very little free acid remains. Water (450 cc.) is then added and sodium chloride, depending on the silver and mercury present. With Anaconda material (80 to 100 mg. Ag and 250 mg. Hg), 30 cc. or 0.57 g. NaCl is a safe quantity. The beaker is again heated to boiling to dissolve copper sulphate and coagulate silver chloride. On removing

[1] *Trans.* A. I. M. E., vol. XLVI, pp. 772–786.

[2] *Trans.* A. I. M. E., vol. XXXVI, p. 3; vol. XLI, p. 786.

the beaker, 150 cc. water are added to keep copper sulphate from separating. It may be filtered at once or kept until the next day. The averages from 35 duplicate samples showed

Silver { filtered at once..............85.904 mg.
filtered next day.............86.050 mg.

Assays of 11 samples by different methods gave the results which are averaged in Table XXXI.

TABLE XXXI.—RESULTS BY COMBINATION METHODS

	Gold milligrams		Silver milligrams
	Average of assays as weighed	Average by weighing all buttons together	
Combination, nitric acid water, 1 a. t.	0.2709	0.2655	76.445
Combination, nitric acid mercury, 1 a. t.	0.3000	0.2955	
Combination, sulphuric acid water, 1 a. t.	0.3018	0.2955	
Combination, sulphuric acid mercury, 1 a. t.	0.3064	0.2991	76.545
All fire, 0.1 a. t.	0.3091	0.2973	

The treatment of the filter containing the gold and silver does not differ from that used in the nitric-acid method—scorifying with test lead after cautiously burning the paper.

A peculiarity of this method is that with some low-grade bullions none of the silver is dissolved, and on adding sodium chloride no precipitate of silver chloride forms. No antimony, arsenic, selenium, or tellurium remains insoluble with the precious metals.

Combination Assay for Matte.—Van Liew's method of treating in the cold is rarely suitable for mattes, as heat is usually essential in order to insure a decomposition of the matte in a reasonable length of time. Take[1] duplicates of 1 assay ton each and treat in large beakers, provided with watch-glass covers, with 100 cc. of distilled water and 50 cc. HNO_3 (sp. gr. 1.42). After the

[1] "Assay of Copper and Copper Matte," *Trans.* A. I. M. E., vol. XXV p. 258.

violent chemical action subsides, add 50 cc. more of concentrated acid, and warm the beakers on a hot plate until everything soluble is dissolved: usually the residue is white or grayish. Next, evaporate a considerable part of the acid by boiling, expelling all of the nitrous fumes, dilute to 500 cc., add 3 cc. of concentrated H_2SO_4, 10 cc. of saturated lead-acetate solution, and enough salt solution of the strength mentioned for blister copper to precipitate the silver; then stir briskly and let them stand over night. Next morning, warm the solutions on a steam bath and filter through rather thick filter paper or a double paper. Filtrates must be perfectly clear and free from suspended $PbSO_4$. Wash beakers and residue thoroughly with hot water, dry the filters in an air bath, and then wrap them up in about 8 g. of sheet lead and scorify with 40 g. of test lead and 1 g. of borax glass. Cupel the buttons with feather litharge. Reassay the slag from the scorification and the cupel and add the resultant gold and silver to the assay.

When heavy copper ores, which are apt to leave large amounts of siliceous residue, are to be assayed by this method, the general method for mattes is followed, except that the residues after filtering and drying are treated as follows:

Take a 20-g. crucible and place in it 1 assay ton of PbO; then put the filter paper containing the residue on top of this, place the crucible in the mouth of the muffle at a low heat, burn off the filter paper until the flame subsides, remove from the muffle, put a cover on the crucible, and allow to cool. When cold, add 0.5 assay ton PbO, 15 g. Na_2CO_3, 2 g. argol, mix well with a spatula, and put on a cover of borax glass. Then proceed as in the ordinary assay.

General Precautions to Be Observed in the Combination Assay. The combination methods on copper material agree well with the standard scorification methods for the same material when correction of cupel loss is made for the latter method. The scorification methods will often seem to give higher results, but this is, in most cases, due to the fact that the silver beads frequently contain from 2.5 to 4 per cent copper. The combination method gives, in most cases (Van Liew's method possibly excepted), uniformly lower results in gold (4 per cent) than the standard corrected scorification method. This is generally ascribed to the formation of nitrous acid (HNO_2) during solution, which, in connection with nitric acid, is said to have a solvent action on

gold; but such authorities as W. F. Hillebrand[1] dispute this. The solution may be due to the formation of H_2SO_4 during solution, as the mixture of this acid and HNO_3 has a solvent action, or to the presence of impurities like chlorides or HCl, etc., or, possibly, to the presence of nitrates, particularly those of iron or copper.

It has been demonstrated that gold is very slowly soluble in hydrochloric-acid solutions of iron alum, ferric sulphate, and cupric chloride, but not in pure HCl.[2]

The fact that the combination method on copper-bearing material gives low results on gold is, however, well established.

Owing to the number of manipulations in the combination assay, it is often apt to give low results in the hands of inexperienced chemists, mainly due to the mechanical losses in handling. The directions given should be carefully followed, especially those regarding amount of solution, strength of acid, temperature, time, etc. Neatness is indispensable. The HNO_3 must be pure. The directions regarding the burning off of the filter paper must be closely followed. The amount and strength of the salt solution must be carefully adhered to and it must be added at the proper time. Some assayers, instead of adding salt solution at the same time as H_2SO_4 and $Pb(C_2H_3O_2)_2$, filter off the residue containing the gold and make a separate precipitation for the silver, believing that the addition of a salt solution may cause a slight redissolving of the gold. At this point of the assay, that is, however, hardly probable. A large amount of NaCl is to be avoided, as AgCl is very appreciably soluble in brine. Cabell Whitehead recommends NaBr or KBr instead of NaCl for this reason, but Edward Keller states that it is not superior.

Combination Method for Precipitates from the Cyanide Process.[3]—Where the troublesome base-metal impurity is zinc instead of copper, as in this case, sulphuric acid or, preferably dilute hydrochloric can be substituted with advantage for HNO_3. The method is as follows:

Of the precipitates, 0.10 assay ton is taken, placed in a beaker, and 20 cc. of sulphuric acid (concentrated) and 60 cc. of water

[1] Hillebrand W. F., and E. T. Allen, "Comparison of a Wet and Crucible-fire Methods for Gold Telluride Ores," U. S. Geol. Survey, *Bull.* 253.

[2] McCaughey, W. J., *Jour. Am. Chem. Soc.*, vol. XXXI, p. 1261.

[3] Fulton and Crawford, "Notes on Assay of Zinc Precipitates Obtained in the Cyanide Process," *School Mines Quart.*, vol. XXII, p. 153.

are added. This is heated on a hot plate for about 1 hour or until zinc and zinc oxide are in complete solution. Add salt solution of the strength already mentioned in the paragraph on Van Liew's method for blister copper, in slight excess, to precipitate the silver present, remembering that 1 cc. will precipitate 1 mg. of silver. Stir briskly with glass rod to agglomerate the silver chloride formed.

The residues are then filtered through the proper-sized filter, carefully washed with hot water into the point of the filter paper, and dried in the air bath at a low heat. After drying, transfer to a 20-g. crucible containing 1 assay ton of litharge, and burn the filter paper off in the manner already described. Then add 15 g. of soda and 2 g. of argol, mix thoroughly, and cover with a heavy cover of borax glass. Fuse and cupel the resultant lead button. Weigh the gold and silver bead, and from a preliminary assay determine the proper amount of silver necessary in order to inquart the bead. The amount of silver should be just about 2.5 times the amount of gold. Roll out the bead, after flattening with a hammer, until, after repeated rollings, the fillet will have about the thickness of a visiting card. It is best to anneal the bead at a red heat between the various rollings, in order to prevent cracking on the edges. Then part in a parting flask in hot nitric acid having a specific gravity of 1.26. Boil twice for at least 20 min. each time, in order to insure the complete removal of the silver. This method of parting leaves the gold in one coherent mass, termed a *cornet*, and is identical with the method practiced in the gold-bullion assay.

CHAPTER XI

SPECIAL METHODS OF ASSAY

Telluride Ores.—Gold ores containing the precious metals in the form of tellurides of gold and silver, mainly calaverite and sylvanite, are more difficult of assay than ordinary gold ores, and special methods are essential in order to get good results. The scorification assay is not reliable for telluride ores, giving almost uniformly low results. It is not used by assayers and chemists of the great telluride ore district in Colorado—Cripple Creek. It seems that in scorification the main cause of loss is volatilization, for while the slag loss is higher than for ordinary ores, slag and cupel corrections still leave the results from this assay far below those of the crucible assay when the latter is properly performed.

Of recent years, selenium gold ores have been found,[1] and, in general, the precautions necessary for the assay of telluride ores apply also to selenium gold and silver ores.

Tellurium has a great affinity for gold and silver, that for silver being greater than that for gold; and if a high-grade telluride ore be assayed, even by special method, the beads from the cupellation will frequently still contain tellurium.[2] In the crucible assay, the losses, which are somewhat greater than in ordinary ores, occur in the slag and from the presence of the Te in the lead button, causing absorption of precious metals by the cupel. The aim in the crucible assay is to remove the tellurium from the gold and silver and slag it. This is best accomplished by the presence of considerable litharge as an oxidizing agent and otherwise properly balancing the flux. The flux recommended quite generally by Cripple Creek assayers is made up as follows:

	Parts		Parts
Potassium carbonate	7	Flour	1.0
Sodium carbonate	6	Litharge	30.0
Borax glass	5.5		

[1] "Selenium Gold Ore," *Eng. Mining Jour.*, vol. XC, p. 418; *Mining Sci. Press*, vol. C, p. 224.

[2] Woodward, E. C., "Cupel Losses in Telluride Ores," in *Western Chem. Met.*, vol. I, p. 120.

This is for the ordinary siliceous Cripple Creek ores. About 75 g. of this flux is used with 0.5 assay ton of ore. This gives the following charge:

Ore	0.5 a.t.	Borax glass	8.5 g.
PbO	45.5 g.	Na_2CO_3	9.0 g.
Flour	1.5 g.	K_2CO_3	10.5 g.

The heat recommended is such that a temperature of 1063° C., the melting point of gold, is reached at the mouth of the muffle. Some assayers recommend a somewhat greater temperature to insure the decomposition of the tellurides. The time of fusion should be about 45 to 50 min.

In most telluride ores, the silver contents are not great enough to permit of the parting of the bead obtained from cupellation. It is, therefore, necessary to add silver at some stage before parting, and in this instance it is best done during the crucible assay, since by doing this there is apt to be less absorption of gold during cupellation on account of the presence of silver in the lead button.

It is essential to recognize that the flux recommended above for tellurides does not make what can be strictly termed an *excess-litharge charge*.

Hillebrand and Allen[1] recommend the following charge for Cripple Creek ores (soda ash being here substituted for bicarbonate):

Ore	1 a.t.	Borax glass	10g.
Na_2CO_3	20 g.	Reducing agent (if necessary)	
PbO	180 g.	Salt cover	

This approaches more nearly the excess-litharge charge.

The salt as a cover may with advantage be replaced by litharge or borax. The fusion should be conducted slowly and at a temperature not exceeding 950° to 1000° C.

It is essential in telluride ores to have the sample crushed to 120 or, better, to 200 mesh. The reason for this is that, owing to the irregular distribution of values in these ores, fine crushing is required to get a true sample and, also, because the low melting point of the charge usually employed makes this essential.

The precise behavior of tellurium in the crucible assay, and during scorification or cupellation, has not as yet been investigated

[1] "A Comparison of a Wet and Crucible-fire Methods for the Assay of Gold Telluride Ores," U. S. Geol. Survey, *Bull.* 253.

with scientific thoroughness, though much preliminary work has been done.[1] The following facts are reasonably well established:

1. The great affinity of tellurium for gold and silver, resulting in tellurium's passing to the lead button with the precious metals, unless a charge be used that is essentially oxidizing in its character, and effecting the slagging of the tellurium.

2. During the oxidation of the lead button by cupellation or scorification, the tellurium tends to concentrate in the remaining lead-gold-silver alloy, although in different degree in the two operations, the concentration being more pronounced in scorification.

3. The effect of tellurium on the lead-gold-silver alloy is very greatly to decrease its surface tension, so much, in fact, that if proportionately sufficient tellurium be present the surface tension is changed sufficiently to cause the alloy to "wet" the cupel and be absorbed as alloy, thus causing heavy losses of precious metals. If the proportion of lead to tellurium to gold should attain the concentration of 10:1:1, complete absorption may take place, leaving no gold bead. Such a result will, however, occur only in exceptional cases, as in the direct cupellation of telluride mineral, etc. The accompanying data, due to S. W. Smith, show the relative elimination of tellurium during cupellation and scorification. Lead buttons of 20 g. containing 0.05 g. each of gold and tellurium were submitted to cupellation and scorification, and the process interrupted at intervals for the determination of tellurium.

Table XXXII.—Showing Elimination of Tellurium during Cupellation and Scorification

Cupellation			Scorification		
Cupelled down to weight, grams	Per cent of original lead remaining	Per cent of tellurium in the button	Scorified down to weight, grams	Per cent of original lead remaining	Per cent of tellurium in the button
20.00	100.00	2.48	20.00	100.00	2.48
11.86	59.00	3.25	6.145	30.7	5.94
4.25	21.00	2.49	2.085	10.4	12.90
1.635	8.15	1.80			

[1] Smith, S. W., *Trans.* I. M. M., vol. XVII, pp. 463–476, 1908; Holloway, G. T. and Pearse, L. E. B., *Trans.* I. M. M., vol. XVII, p. 171, 1907 and 1908.

It will be noted that during cupellation the tellurium at first concentrates in the lead and then begins to be eliminated, the percentage decreasing. In the case of scorification, there is a very decided concentration of tellurium in the lead toward the end of the operation. The difference is probably due, in large part, to the fact that in cupellation the tellurium is, in part, absorbed by the cupel as a lead-tellurium alloy, which action cannot take place in scorification. The removal of tellurium by oxidation from lead, thus passing into cupel or slag, is evidently a difficult process. In an alloy of lead, gold, and silver and tellurium, the tellurium can form compounds with both the precious metals and lead. It will be distributed between the two according to the relative masses present and the relative chemical affinities. If, then, in the alloy relatively much lead be present (100 to 200 parts Pb per part Au and Te), by far the larger part of the tellurium will be eliminated by absorption as lead telluride, and only a little will stay with the precious metals. This small amount will not be sufficient materially to lessen the surface tension of the bead at the end of the cupellation, and, hence, absorption will be small. If, however, the amount of lead be small so that the relative amount of tellurium and gold is increased, the absorption of the latter may be very heavy.[1] It follows, therefore, that in lead buttons obtained in the crucible assay, which may contain tellurium, it is better to cupel directly in order to avoid heavy absorption in the cupel. Scorification might be resorted to in this case for two reasons: (1) to reduce a large lead button; (2) in the mistaken idea of eliminating tellurium.

From what has gone before it is evident that a large button is not disadvantageous, as it really tends to decrease the absorption of precious metal when tellurium is present.

The preliminary scorification of lead buttons from crucible assays of telluride ores has been shown to give low results.[2] The cause for the almost universally low results on telluride ores by the scorification method is also to be attributed, in part, to the above reasons.

4. Silver seems to exert a protective action on the gold and lessen the absorption of the latter, due, probably, to the greater affinity of silver for tellurium, thus forming silver telluride to the

[1] Rose, T. K., *Trans.* I. M. M., vol. XVII, p. 285. 1908.

[2] Fulton, C. H., *School Mines Quart.*, vol. XIX, p. 419; Smith, S. W., *ibid.*

exclusion of the formation of much gold telluride; consequently lessening the absorption of gold. It is, therefore, desirable to perform the assay in the presence of considerable silver, which will have to be added anyway at a later stage to give a bead that will part.

In the assay of telluride ores, the general object, therefore, will be to remove as much tellurium as possible from the gold and silver before cupellation. This is best done by the performance of a crucible assay with an oxidizing charge. The oxidizing properties of the charge are obtained by the use of an excess of litharge. If we consider the ordinary telluride ore as composed of a siliceous or shaly gangue containing the precious metals as tellurides and containing, also, certain amounts of sulphides, then when this is subjected to fusion with litharge (a large excess), the telluride minerals and sulphides are oxidized, the tellurium probably forming tellurate of lead or, in the presence of soda, tellurate of soda (see "behavior of sulphur," Chap. VI). If, however, an insufficient amount of lead oxide is present so that it forms lead silicates only with the silica of the ore, the oxidizing effect will be much diminished, since lead silicates form at a low temperature and do not readily give up oxygen. It is desirable, therefore, to form a slag which has the characteristics of an excess litharge charge, *viz.*, is not glassy, but of an earthy, dull appearance. Considerable soda should be present to aid the oxidation of the impurities. The borax glass should not exceed 5 to 10 g., and the lead button made should be large—25 to 30 g The fusion should be made slowly, particularly at first, and the temperature not exceed about 1000° C., since there is a possibility of dissociating the tellurium compounds in the slag and sending the tellurium into the lead button.

It is probably impossible to remove all the tellurium from gold and silver by such an oxidizing fusion, for the reason that the reduction of lead from some of the litharge at a certain stage of the assay for the collection of the gold and silver also again reduces some of the tellurium which has been oxidized. It is desirable to obtain the full oxidizing effect of the litharge before the reduction of lead takes place, and for this reason charcoal is to be recommended as the reducing agent, when this needs to be employed, instead of argol or flour, since the CO evolved by the two latter begins to reduce lead from lead oxide at a temperature about 300° C. less than solid carbon, which acts at about 550° C.

For ordinary siliceous telluride ores of only slight reducing power, the following charge is recommended:

Ore	0.5 a. t.
PbO	100.0 g.
Na_2CO_3	30.0 g.
Borax glass	6.0 g.
Charcoal	1.1 g.
Silver foil	10 to 20 mg.
PbO cover	10 g.

The fusion should be conducted slowly at first, the final temperature not much exceeding 1000° C.

If the button from the fusion is thought to contain tellurium, as is probably the case in the assay of a high-grade ore, it will be desirable to place it in a 20-g. crucible, cover with 30 g. PbO, mixed with 2 g. borax glass and bring to fusion, then pour and proceed as usual. This treatment will eliminate considerable tellurium from the lead (S. W. Smith).

It is stated[1] that in the oxidizing roasting of Cripple Creek telluride ores, in their preparation for chlorination or cyanidation, the greater part of the tellurium in the raw ore is found in the roasted ore as a tellurite of iron. Some assayers add an iron nail to the assay, not so much to desulphurize as to provide an excess of iron for the purpose of combining the tellurium with it, as in the case of sulphur.

For the quantity of tellurium present, its influence on the assay is certainly profound. The following table gives an idea of the quantity present:

Table XXXIII.—Quantity of Tellurium in Ores

Element	Cripple Creek ore, per cent	Black Hills Cambrian, per cent
Tellurium	0.0742, 0.092	0.0033, 0.010
Gold	0.0506, 0.060	0.0026, 0.003
Silver	0.0075, 0.0103	

As already stated, tellurium is with difficulty separated from gold and silver and in spite of an oxidizing charge is frequently carried down in the lead button. The loss then takes place in the cupel, tellurium causing a heavy absorption. Some loss,

[1] Rickard T. A. *Trans.* I. M. M., vol. VIII, p. 108.

however, takes place by volatilization. There is, also, a somewhat higher slag loss in the telluride assay than in the assay of ordinary ores.[1] Hillebrand and Allen, already quoted, assayed telluride ores by the combination wet-and-dry assay, getting the gold and silver free from tellurium, but found that the crucible assay as ordinarily performed for telluride ores gave just as satisfactory, if not better, results.

A Study of the Assay of Black Hills Cambrian Ores.—These ores are probably complex tellurides. They were oxidized and of the following average composition:

SiO_2 = 71.5 per cent; Fe_2O_3 = 16.3 per cent; Al_2O_3 = 4.8 per cent;

CaO = 1.5 per cent; Gold = 0.79 oz.; Ag = 0.10 oz.

Samples of this type of ore, representing controls on car-load lots, were assayed by assayers A and B in the same laboratory, with the same kind of cupels and with great regard to temperature of cupellation. Assayer A made fusions on 1-assay-ton lots, in triplicate, using 4 assay tons of the stock flux *A*, with a quite heavy borax glass cover, fusing at about 1100° C. and parting with acid diluted 1:9. Assayer B made quadruple assays of 0.5 assay ton of the same pulp samples, using 3 assay tons of stock flux *B*, with a soda cover ¼ in. thick, parting with 1:4 acid. As the quantity of silver present was negligible, all assays were salted with silver. In each case, the gold beads were weighed singly and required to check each other in weight, then weighed together and the combined weight divided by 3 or 2 to obtain the ounces gold per ton.

Assayers A and B then exchanged fluxes, and as they checked each other's previous results closely, it became evident that the flux of assayer A was ill balanced and would not give good results. Slag and cupel corrections were made by Assayer A on assays made with his flux, but even these corrections added failed to bring his results up to those of assayer B.

The question arises as to what is the specific trouble with flux A. On examination, it will be found to contain an excessive amount of borax glass, especially when the cover is considered. It is very probable that the acidity of the charge (although a good fluid slag is obtained) is so great, taking into account both the

[1] Fulton, C. H., *School Mines Quart.*, vol. XIX, p. 419; Smith, F. C., *Trans.* I. M. M., vol. IX, p. 344; *Mining Rept.*, vol. LI, p. 163; Hillebrand and Allen, U. S. Geol. Survey, *Bull.* 253.

TABLE XXXIV.—ASSAY OF BLACK HILLS CAMBRIAN ORES

	Assayer A, parts	Assayer B, parts
Stock flux:		
Sodium carbonate	3.25	3.25
Potassium carbonate	2.25	2.25
Litharge	18	22
Borax glass	5	2
Argol	1	0.75 to 1
Charge:		
Ore	1 a. t.,	0.5 a. t.,
Sodium carbonate	13 g.	9g.
Potassium carbonate	9	6.5
Litharge	73	63
Borax glass	20	6
Argol	4	2 to 3
Cover	Borax glass	Sodium carbonate
Results of assays:		
Lot number	Ounces gold per ton	Ounces gold per ton
88,870	0.74	0.78
88,832	0.80	0.83
88,874	0.71	0.80
88,823	0.82	0.98
88,721	0.80	0.88
88,851	0.85	0.89
88,818	0.85	0.91
88,940	0.79	0.84
3,669	0.82	0.91
88,853	0.85	0.91
88,890	0.81	0.83
71,957	0.79	0.82
88,826	0.77	0.82
3,843	0.77	0.81
88,780	0.80	0.88
22,522	0.66	0.73
98,509	0.69	0.79
22,050	0.50	0.58

silica of the ore and the borax glass, that the ore is not completely decomposed by the basic ingredients of the charge; *i.e.*,

the soda and litharge become saturated with borax and then do not completely decompose the siliceous ore. The fact that reassays of the slag do not bring the results up to the figures obtained by assayer B does not necessarily imply that the slag does not contain these values, as the charge used to flux the slags and cupels again contains much borax glass, so that practically the same conditions obtained as before.

The Assay of Copper-bearing Material.—Copper-bearing material includes ores containing copper and furnace products, chiefly mattes, blister copper, etc. Copper, which in the assay has a strong tendency to go into the lead button, causes, when present in sufficient quantity, serious losses by cupel absorption. All methods of assays for this class of material, therefore, endeavor to eliminate copper from the lead button to be cupelled. A standard method for the assay of material high in copper, especially for Ag, is the combination assay for blister copper and mattes, described in Chap. X.

Another standard method, especially for gold, and one that is carried out frequently as a check to the above, is the scorification or *all-fire* method. This is performed as follows:

Ten samples,[1] of 0.10 assay ton each, are taken and placed in 3-in. scorifiers with 50 g. of test lead (the silver content of which is accurately known); 25 g. of the lead are mixed with the matte, or borings, etc., and the other 25 g. used as a cover. On top of the charge is placed 1 g. each of silica and borax glass. The scorification is carried on at a moderate temperature until the assays are just about to slag over, which takes usually about 25 min., and then they are poured. The resultant button will weigh about 15 to 16 g. and be quite hard with copper. The buttons, cleaned from slag, are scorified, test lead being added to make the total lead up to 40 g. The second scorification will take about 30 min. and the resultant buttons will weigh from 10 to 12 g. These are cupelled in 10 separate cupels, placed so as to be subject to uniform temperature, *i.e.*, in one horizontal row across the muffle. Cupellation should be conducted at a temperature as low as is feasible.

The beads are weighed separately and then together. They are then grouped in two lots of five each, which are parted in acid, strength 1:9, the beads being kept in this acid at nearly

[1] A good plan is to start with 12 samples, allowing for the possible loss of 1 or 2, to insure the probability of at least 10 successful results.

boiling temperature for 20 min. and finished for 5 min. with 1.42 sp. gr. acid (full strength). The ten cupels are taken in lots of two each (only the litharge-stained part is taken), crushed to pass 100 mesh, and assayed by the following charge:

100 g. PbO	45 g. borax glass
20 g. Na_2CO_3	3 g. argol
Soda cover	

The lead buttons are cupelled, and the silver and gold obtained added to the first weights. The scorification slags may also be reassayed and this correction added, but in practice the cupel correction is the only one usually allowed. Sometimes, no correction is allowed. It is to be noted that, even with a rescorification of the first button of the assay, the final silver beads, from 55 per cent Cu matte containing 180 oz. Ag per ton and 2.31 oz. gold, will contain from 2.5 to 4 per cent copper, which must be deducted in order to get correct silver results. (For a further discussion of scorification slag losses and cupel absorption in assaying copper-bearing material, see Chap. XII.)

The scorification method is generally employed for the determination of gold in mattes, and the combination method for the determination of silver. Of recent years, special crucible methods for copper mattes and copper-bearing material have been developed with considerable success.[1]

A satisfactory method on copper mattes, up to 20 per cent copper and high in gold and silver, was practiced by the Standard Smelting Company, at Rapid City, S. Dak. The matte sample was put through a 120-mesh screen, and for controls four assays of 0.25 assay ton each were made, with the following stock flux:

	Parts		Parts
Silica	11	Sodium carbonate	25
Litharge	70	Niter	5

An 0.25 assay ton matte was run with 3.5 assay ton flux and a thin borax glass cover. The flux figured to the charge was as follows:

0.25 a.t.	matte	24.0 g	Na_2CO_3
10.5 g	SiO_2	5.0 g	KNO_3
67.0 g	PbO		

[1] "An All-fire Method for the Assay of Gold and Silver in Blister Copper," *Trans.* A. I. M. E., vol. XXXIII, p. 670; Perkins, "The Litharge Process for the Assay of Copper-bearing Ores," *ibid.*, vol. XXXI, p. 913.

The heat used was high and the fusion short, giving a clean fluid slag and a bright button of approximately 20 g. These buttons were cupelled directly for gold and silver. One cupel was then run with the corresponding slag in the same crucible that the original fusion was made in, and the result of the four corrections added to the sum of the original buttons. No scorification was made before cupellation. The average correction, on the usual grade of matte (5 oz. Au, 40 oz. Ag), was 2.5 per cent gold and 5.5 per cent silver. Below is a comparison of this method with the standard scorification assay, including cupel and slag correction. The copper content of this matte was 19.98 per cent.

Table XXXV.—Comparison of Methods in Assay

	Crucible method, ounces		Scorification method, ounces	
	Gold	Silver	Gold	Silver
Original assay	4.10	36.24	3.90	35.07
Correction	0.10	1.00	0.25	1.95
Total	4.20	37.24	4.15	37.02

The returns on this pulp by the refiner were: gold, 4.19 oz.; silver, 36.71 oz.

Table XXXVI.—Comparison of Methods in Assay
Copper 17.6 Per Cent

	Crucible method, ounces		Scorification method, ounces	
	Gold	Silver	Gold	Silver
Original assay	3.42	31.94	3.40	31.86
Correction	0.10	1.85	0.11	1.93
Total	3.52	33.79	3.51	33.79

The following table shows results by this method with correction and refiners' results (by same method without correction):

TABLE XXXVII.—CORRECTED AND UNCORRECTED ASSAYS ON COPPER MATTE

Lot number	Crucible method: Standard Smelting Company, ounces per ton corrected		Crucible method: refiner. ounces per ton uncorrected	
	Gold	Silver	Gold	Silver
1,391	17.73	75.4	17.67	74.13
1,404	17.75	73.5	17.625	72.42
1,412	11.35	45.7	11.145	42.95
1,435	10.02	39.9	10.065	39.08
1,450	9.10	44.6	9.02	43.01
1,457	6.89	48.75	6.815	46.28
1,458	9.95	58.37	9.935	52.31
1,470	8.235	50.86	8.24	52.31
1,471	4.845	40.52	4.87	39.48
1,484	7.34	45.04	7.265	44.68
1,489	6.45	47.98	6.83	46.67
1,500	5.78	45.34	5.84	45.06
1,503	4.61	27.11	4.58	26.51
1,513	3.815	32.75	3.80	31.55
1,525	3.12	39.62	3.205	33.84
1,529	3.10	33.00	3.36	31.14
1,533	4.20	37.24	4.19	36.71

A typical sample of matte on which these assays were made analyzes as follows:

Gold............	4.10 oz. per ton	Silica...............	3.3 per cent
Silver...........	31.55 oz. per ton	Lime...............	0.5 per cent
Copper..........	17.4 per cent	Sulphur.............	29.1 per cent
Iron.............	45.9 per cent	Lead...............	trace
Zinc............	2.5 per cent		

The crucible charge employed can readily be modified to apply to mattes higher in copper or greater in reducing power.

Perkins' excess-litharge method has already been described. He states that for low-grade copper-bearing material (2 to 4 per cent), 150 g. of PbO to 0.5 assay ton of ore will remove most of the copper, if the balance of the fluxes is properly proportioned, *i.e.*, if there is ample free PbO to dissolve copper oxides. For high-grade mattes, etc.—48 to 60 per cent copper—8 assay tons of PbO to 0.1 assay ton of matte will remove most of the copper. Perkins also developed a crucible method for metallic copper, as follows:

Weigh out 12 lots of copper borings each 0.1 assay ton, and place in 20-g. crucibles. Into each crucible put 800 mg. of powdered sulphur, mix thoroughly with the copper, and then on top of this put the following flux, being careful not to mix the flux with the copper:

	Grams		Grams
Na_2CO_3	8	PbO	240
K_2CO_3	8	SiO_2	15

Salt cover

Place the crucibles into a dark-red muffle and gradually raise the temperature for 45 min. to a yellow heat. The temperature regulation is important, and it is necessary to produce a neutral or reducing atmosphere in the muffle by the presence of coal or coke. The buttons, weighing about 18 g. each, are put together in lots of three, representing 0.30 assay ton, and scorified at a low heat. The resultant buttons should weigh 5 to 6 g. Each of these buttons is now rescorified with 25 g. of lead at a low heat, until 6-g. buttons are obtained. These are cupelled with feathers. This method is stated to give results on gold equal to the all-scorification method and on silver equal to the combination method.

The Assay of Zinciferous Ores and Metallurgic Products Containing Zinc.—Zinc most frequently occurs in ores as the sulphide (sphalerite) sometimes as oxide, carbonate, or silicate. In certain metallurgical products, zinc cyanide precipitates, and the crusts from Parkes' process, it is present as the metal. Zinc boils at 940° C. and rapidly volatilizes. Zinc oxide volatilizes slowly at 1180°, and rapidly at 1400° C. Zinc silicates alone are difficultly fusible but are readily so when mixed with borax or boric acid or ferrous silicate.[1] The presence of zinc in material to be assayed calls for certain precautions, and, in general, the assay is difficult. Metallic zinc has a great affinity for gold and silver, greater than lead, as is shown by the Parkes' process for the desilverization of lead bullion. Under oxidizing influences,[2] the formation of zinc oxide and its volatilization cause losses of gold and silver. That this loss is mechanical does not make it less serious. The boiling point of zinc occurs at a temperature

[1] Rose, T. K., "Refining Gold Bullion, etc., in Oxygen Gas," *Trans.* I. M. M., vol. XIV, p. 377, 1905.

[2] Williams, *Proc.* Chem. Met. and Min. Soc. S. Africa, vol. III, p. 132.

somewhat below the normal for ordinary scorification, and it is this fact, coupled with the fact that the zinc oxide formed is with difficulty soluble in litharge, that makes accurate assay results hard to obtain, especially in scorification. Zinc containing gold and silver may be distilled off and volatilized with very little loss of gold and silver, if the conditions are reducing.[1]

Scorification is frequently employed for zinciferous ores, although it is not generally satisfactory. When used, it is best carried out in a way similar to that adopted for copper-bearing material, using from 0.05 to 0.10 assay ton of ore with from 50 to 80 g. of test lead, 2 g. of borax glass, and 1 g. of silica, the last being essential to flux the zinc oxide formed. Otherwise, insoluble scoria and crusts form on the scorifier. Slag and cupel corrections are generally necessary and from 5 to 10 assays are made, the results being averaged. As zinc is readily oxidized, lead buttons contaminated with zinc are not to be feared, and rescorification is rarely necessary.

Among the most important zinciferous materials presented for assay are the zinc-gold precipitates from the cyanide process. Scorification is not desirable for these.[2] They are best assayed by the crucible method or by one of the combination methods already described.

Crucible Method.—The crucible method best suited for unoxidized zinc ores is the niter one, with sufficient silica present to form at least the monosilicate with zinc. Borax glass and much litharge is also desirable. On a practically pure sphalerite, the following charge will give good fusions at temperatures of about 1100° C.:

Ore	0.5 a.t.	SiO_2	8 g.
Na_2CO_3	15 g.	KNO_3	22 g.
PbO	150 g.	Heavy borax glass cover.[3]	

This charge can be modified, as regards niter and silica, to suit any sphalerite ore.

A good crucible charge for cyanide precipitates, containing up to 50 per cent zinc, is

[1] Rose, *ibid.*, and references.

[2] "Notes on the Assay of Zinc Precipitates, etc.," in *School Mines Quart.*, vol. XXII, p. 153.

[3] A similar charge is recommended by Lay, for complex zinc-lead concentrate; see *Mineral Ind.*, vol. XIII, p. 287.

Precipitates	0.1 a.t.	SiO_2	5 g.
Na_2CO_3	5 g.	$Na_2B_4O_7$	2 g.
PbO	70 g.	Flour	1 g.

Light borax glass cover

The following method [1] is used on cyanide precipitates containing 12,000 to 22,000 oz. Ag and 300 oz. Au per ton at the mill of the N. Y. and Honduras Rosario Mining Co. in Honduras, Central America.

In a 20-g. crucible, mix 27 g. test lead, 2.5 g. borax glass, 0.5 g. silica with 0.1 a. t. of the precipitates, tapping the crucible to make certain that no material adheres to the sides. In another crucible, mix 33 g. PbO, 25 g. Na_2CO_3, 4.5 g. borax glass, 1.5 g. silica, and 0.15 g. charcoal. After mixing, transfer this second charge on top of the contents of the first crucible, and make the fusion as usual. The button separates very cleanly from the slag. The slag and cupel are reassayed, and one weighing made on the three beads recovered from the cupellation. The slag corrections are small, amounting to about 25 oz. Ag per ton of precipitates containing 14,000 oz. The gold loss in the slag is very small.

The assays are run in triplicate. In the assay of such high-grade material, weighing of precipitates must be done on analytical balances.

Assay of Plumbago Crucibles for Gold and Silver.—Graphite or plumbago crucibles are extensively used in the smelting of cyanide-zinc precipitates, and the old discarded ones are usually sold in lots to some smelter; they often contain considerable gold and silver. These pots present difficulty in assaying, chiefly on account of the graphite and zinc contained. From a given weight of sample, the metallics and scales are separated by passing the material through a 150-mesh screen, and a regular scale assay is made as outlined at the end of this chapter. The pulp is assayed as follows:[2]

From 0.05 to 0.10 assay ton is taken and mixed with a little more than one-half its weight of niter and 30 g. of litharge, placed in a 2.5-in. scorifier, covered with 30 g. of litharge and afterward with a thin cover of borax glass, placed in a muffle,

[1] SMITH, E. VAN L., Private communication. Name of the originator of the method not known to the authors.

[2] A modification of T. L. Carter's method; see *Eng. Mining Jour.*, vol. LXVIII, p. 155.

and fused finally at a yellow heat. The buttons are cupelled, weighed, and parted as usual.

Crucible assays may also be made on this material by the niter excess-litharge fusion, with a charge as follows:

0.1 a.t. graphite	5 g. Na_2CO_3
70 g. PbO	5 to 11 g. KNO_3 (according to carbon contents of pulp)
5 g. SiO_2	

Borax glass cover

In both methods, it is essential that the amount of pulp, usually, should not exceed 0.1 assay ton, the carbon giving difficulties with greater amounts than this.

The Assay of Residues from Zinc Distillation (*Containing Considerable Carbon*) *for Silver and Gold.*[1]—From 0.10 to 0.5 assay ton of the powdered residue is mixed with 35 g. of niter and 10 g. of Na_2O_2 (sodium peroxide) and dropped, in lots of 5 g. each, into a red-hot crucible which can be readily covered, and the oxidation reactions permitted to complete themselves. The flux then added consists of 70 g. litharge, 10 g. borax glass, 10 g. silica, 2 g. argol, and a light borax glass cover. The fusion is carried out at a yellow heat and the buttons cupelled as usual.

The Assay of Antimonial and Arsenical Ores for Gold and Silver.—Gold- and silver-bearing antimonial ores, such as stibnite, jamesonite, etc., are usually assayed by the niter method,[2] in the presence of considerable soda and niter, to induce the formation of the antimoniate of soda. A preliminary assay to determine the amount of niter is essential. The following charge is recommended for nearly pure stibnite:[3]

Ore	0.5 a.t.	KNO_3	18 g.
PbO	120 g.	Borax glass	6 g.
Na_2CO_3	10 g.	SiO_2	10 g.

Salt cover

The fusion should be conducted slowly and at a low temperature. The button will usually contain very little antimony, the cupel not showing scoria or cracks. If it does contain enough to cause losses in cupellation, the buttons should be scorified. Smith[4] gives the following charge for ore containing approxi-

[1] SANDER, K., *Eng. Mining. Jour.*, vol. LXXIII, p. 380.

[2] KITTO, WILLIAM, "The Assay of Antimonial Gold Ores," *Trans.* I. M. M., vol. XVI, p. 89, 1906.

[3] SMITH, E. A., "The Assay of Complex Gold Ores," *Trans.* I. M. M., vol. IX, p. 332.

[4] *Ibid.*

mately 75 per cent stibnite; the niter, etc., can be varied for the ore as the gangue increases:

Ore	1 a.t.	Borax glass	8 g.
PbO	75 g.	KNO_3	20 to 25 g.
Na_2CO_3	25 g.	Salt cover	

Another method, practically as good as the niter method, is the roasting with charcoal or coke dust.[1] The sample of ore, usually 1 assay ton, is mixed with approximately its own volume of coke dust or coal dust, placed in a 5-in. roasting dish, covered with another dish, and roasted in a muffle with closed door, at a temperature not exceeding a dark cherry red (635° C.), for about 35 to 40 min. This will cause the volatilization of 95 to 96 per cent of the antimony as sulphide without appreciable loss of gold. The roast should have a yellow appearance when finished and can be fused with the following charge:

Roasted ore		SiO_2	7 g.
PbO	70 g.	Argol	2 g.
Na_2CO_3	20 g.	Borax glass cover	

This method gives good results on jamesonite ores.

Arsenical ores are assayed by the same methods as the antimonial ores; also by the iron-nail method, although this last is not generally to be recommended. The subject of the best method of assay of antimonial and arsenical ores still lacks thorough investigation. The chief points may be outlined as follows:

1. In the roasting, unless great care is taken as regards temperature, mechanical loss of gold and silver takes place, owing to the rapid disengagement of the arsenic and antimony oxides or sulphides of these metals. Unless the roast is conducted at a low heat and in the presence of considerable carbon, arseniates and antimoniates of base metals or silver may form, holding values which later on are not completely decomposed in the crucible, owing to their stability at a high temperature, the result being appreciable slag losses.

2. In the niter method, the presence of much niter, with its powerful oxidizing effect, may also induce the formation of arseniates and antimoniates, containing silver and possibly gold, which will remain in the slag.

[1] Sulman, *Trans.* I. M. M., vol. IX, p. 340.

3. In the iron-nail method, unless the fluxes are carefully adjusted and the temperature kept below 1100° C., speiss carrying values is very apt to form above the lead button and thus necessitate a reassay or a treatment of this speiss.

The Assay of Arsenical Nickel-cobalt Silver Ore.[1]—Two types of ores may be considered: (*a*) Those high in Ag and also high in Ni and Co contents, and (*b*) those low in Ag but high in Ni and Co contents. It is essential to flux the Ni and Co in the slag, since these elements seriously interfere with cupellation, causing low results. Ni present in the lead button to the amount of 0.5 per cent causes a scum of NiO to be left on the cupel. More than this causes the "freezing" of the button. The effect of cobalt is not so pronounced as that of nickel.

For the ores high in silver, the scorification assay is to be recommended with the following charge:

Ore	0.05	to	0.10	a. t.
Lead	65	to	75	g.
Borax glass	3	to	5	g.
Silica	1	to	3	g.

Slag and cupel corrections should be made. It is desirable, at times, to check results by wet analysis for silver.

For ores low in silver, the crucible assay with high litharge gives better results than the scorification assay. Small amounts of ore, 0.10 to 0.2 a. t., should be used, for the nickel, cobalt, and arsenic in the ores are apt to form a speiss in the assay. For ores containing metallic silver in any amount, the "scale assay" should first be made.

The Assay of Sulphides, Mainly Pyrite, but Containing Small Amounts of Copper, Zinc Sulphides, Etc.—Where gold only has to be determined in ores of this character, the roasting method is satisfactory. This, however, proves unreliable for silver, and in many cases (as at Leadville) the silver contents of these sulphides were the most important. The best method, after many trials, was found to be the niter fusion on comparatively small lots of ore. The Leadville ore had the following analysis:

	Per Cent		Per Cent
Iron	33 to 44	Zinc	4 to 8
Sulphur	38 to 45	Copper	0.5 to 3.5
Insoluble	4 to 20	Lead	0 to 0.4

[1] Bullens, D. K., *Eng. Mining Jour.*, vol. XC, p. 809; Lodge, *Trans. A. I. M. E.*, vol. XXXVIII, p. 638.

Four assays were made on 0.25 assay ton each, with 3 to 4 assay tons of the following flux, the amount depending on the reducing power, *i.e.*, on the amount of sulphides present:

	Parts		Parts
PbO	16	SiO_2	3
KNO_3	3	Borax glass	3
Na_2CO_3	6		

Either a salt or a soda cover was used. The temperature of fusion was brought up gradually to a yellow heat. With 4 assay tons of flux, this gives the following charge:[1]

Ore	0.25 a.t.	Na_2CO_3	22 g.
PbO	60 g.	Borax glass	11 g.
KNO_3	11 g.	SiO_2	11 g.

The buttons were usually clean and separated well from the slag.

Another method which may be used on ore of this type is the niter-iron method. This has the advantage that no preliminary assay is necessary to determine the amount of niter for the proper-sized button but that only sufficient niter is added partially to oxidize the sulphides, the iron nails being relied upon to decompose the balance of the ore. On ores of the class shown by the analysis, the following charge is successful:

Ore	0.5 a.t.	SiO_2	8 g.
Na_2CO_3	25 g.	Borax glass	8 g.
PbO	30 g.	Iron nails	two to three 10 d.
KNO_3	15 g.	Thin borax glass cover	

If the ore has a lesser reducing power than shown by the analysis given, niter and silica should be decreased in the charge.

Rapid Methods for Sulphide Ores.[2]—In using the niter method to oxidize sulphides, a preliminary assay is desirable to determine the proportion of oxidizing agent necessary. After some experience, however, the approximate percentage of sulphides in ores may be estimated quickly by vanning with sufficient accuracy for the addition of the proper amount of niter. An ordinary color or spot plate used in volumetric chemical analysis

[1] See, also, VAIL, W. G., "Niter Assay for Sulphide Ores," *Western Chem. Met.*, vol. II, p. 14.

[2] HAWLEY, F. G., *Eng. Mining Jour.*, vol. LXXXIX, p. 1221; vol. XC, p. 647; also, *Mining Sci.* Press, vol. CI, p. 147; and HALL, E. T., *Mining Sci.* Press, vol. CI, p. 345.

is best used for the vanning. Small quantities of ore are placed in the four outside depressions and carefully vanned in a basin of water until only the sulphides are left. The quantity of these is estimated in percentage of the total amount of ore taken for the vanning test. In gaining experience with this method, it may be desirable for the assayer to make comparisons with ores of known sulphide contents. If pyrite be taken as the sulphide of unit reducing power, then chalcopyrite, blende, pyrrhotite, and arsenopyrite will have a reducing power of two-thirds, stibnite of one-half, and galena and chalcocite of one-third that of pyrite. In the complex sulphide ores, the relative amounts of the different sulphides are estimated and the amounts converted into terms of pyrite. In the ordinary excess-litharge charge with a fair amount of borax and soda and with 0.5 a.t. of ore, 15 per cent of pyrite will reduce a 22-g. button. For every 5 per cent of pyrite present above 15 per cent, 2.1 g. of niter are necessary to destroy the excess reducing power. Two stock fluxes are used in the assay of ores: (1) The reducing flux, designed to give a 22-g. button with a neutral ore on a charge of 0.5 a.t. ore and a measure or scoop of flux (84 g.). This flux is made as follows: PbO, 15 parts; Na_2CO_3, 4 parts; borax, 2 parts; flour, 0.44 parts. When 84 g. of this flux are used, it gives the following charge:

Ore	0.5 a.t.
PbO	60 g.
Na_2CO_3	16 g.
Borax	8 g.
Flour	1.75 g.

(2) Non-reducing flux to be used in connection with niter for sulphide ores which will give a button larger than 22 g. This flux is made as follows: PbO, 15 parts; Na_2CO_3, 3.5 parts; borax, 2.5 parts; silica, 0.5 parts. When 84 g. of this flux are used, it gives the following charge:

Ore	0.5 a.t.
PbO	60.0 g.
Na_2CO_3	14.0 g.
Borax	10.0 g.
Silica	2.0 g.
Niter	As necessary

When sulphide ores are assayed which do not contain sufficient sulphides for a 22-g. button, the reducing and non-reducing fluxes are mixed in such proportion as to obtain the correct result.

Thus: Suppose an ore contains 10 per cent pyrite; its reducing power would be $^{10}/_{15} \times 22 = 14.6$ g. lead on the basis of 15 g. or 0.5 a.t. The deficiency in lead is, therefore, $22 - 14.6 = 7.4$ g. In order to obtain 7.4 g. lead, the following amount of reducing flux is required: $^{84}/_{22} \times 7.4 = 28.27$ g. The balance of the charge of 84 g. will be made up of non-reducing flux, and the whole charge will be

Ore	0.5 a. t.
Reducing flux	28.27 g.
Non-reducing flux	55.73 g.

The fluxes and niter are measured by volume in properly designed scoops or measures.

For high-sulphide ores, when very accurate results are required, a preliminary assay is made as follows:

	Grams
Ore	3.64
Non-reducing flux	50.0

This is run in a 10-g. crucible. This charge will give a lead button weighing as much as the niter necessary to oxidize all the sulphides in 0.5 a.t. of the ore. Place the lead button obtained in one scale pan of the pulp scale and from the hook above the other pan suspend by fine wire a weight so that with the wire it amounts to 6 g. Then add niter to the pan having the 6-g. weight until the scale is in balance. This amount of niter is the proper amount necessary to produce a 22-g. button with the ore and the non-reducing flux if 0.5 a.t. of ore is taken for assay (consult Chap. VI).

For important assays, it is desirable to make four assays, combine the buttons from two, and scorify into one button each. Make the two cupellations, weigh the beads separately for silver, combine them for parting, and make one weighing on gold.

If the ores assayed contain more than 12 per cent copper, it is desirable to take the lead buttons from the assay and place them into crucibles with 50 g. of litharge and 2 g. SiO_2, place in the muffle, and leave there 4 or 5 min. after the PbO has melted. Then withdraw the crucible, with the tongs give the contents a rapid swirling motion for a few minutes, and pour. This treatment eliminates most of the copper remaining in the button.

Then cupel and part as usual. It is to be noted that the methods described may have to be modified to suit particular conditions.

Assay of Ores, Etc., Containing Coarse Scales or Metallics.—It is impossible to assay accurately an ore which contains coarse metallic particles, unless the latter are separated by screening, and the gold or silver in them determined independently of that in the finer portion, which is termed *fines*, or *siftings*, the coarse being called *scale* or *metallics*. In the laboratory, a sieve of 100 or 120 meshes per inch, or even finer, is commonly employed, but it is occasionally necessary to use coarser screens for this purpose at intermediate stages of sampling.

The calculation of the average value of the entire sample is a simple one in principle, but its application presents difficulties to some people.

Any convenient weight is taken for screening, preferably, an exact number of grams or assay tons. Such quantities as 100, 200, or 300 g., or 10 or 20 a.t., are suitable to start with when circumstances permit.

The resulting scale is weighed, the weight of fines often being determined by difference, though it is preferable to weigh them as a check; dust loss is usually counted as fines.

If the amount of scale is small, it is wrapped in sheet lead and cupelled directly, or it may be scorified and cupelled, the button parted, and gold and silver weighed. If large enough, several samples of $\frac{1}{20}$ a.t. may be taken and assayed. The fines are assayed as usual.

Several methods of calculation are in use.

Method 1.—The most obvious, and, in many cases, the best, method of calculation is to begin by computing the value per ton of scale in ounces or dollars, to correspond with the assay of the fines, and also to determine the percentage weight of each.

$$S = \text{percentage weight}$$
$$s = \text{assay value per ton of scale}$$
$$F = \text{percentage weight}$$
$$f = \text{assay value per ton of fines}$$

$$\text{Then assay value per ton of original} = \frac{Ff + Ss}{100}$$

Method 2.—This is essentially the one given by Furman in his "Manual of Practical Assaying" and is well adapted for small amounts of scale. Weigh original and scale in grams, calling

weights W and w. Call f the ounces per ton of fines and m the milligrams of gold (or silver) obtained from the total scale. Total ounces per ton of original $= \dfrac{(W - w)f + 29.166m}{W}$

At the Omaha and Grant smelter, the computation is simplified by making $W = 291.66$ g., or 10 a.t., and also weighing w in assay tons.

Method 3.—This is substantially the system advocated by Smoot[1] and Liddell.[2] Determine percentage of scale $= S$. Assay fines as usual. Assay scale and express result as ounces or dollars per ton of scale. Call these results f and s.

(If $w =$ g. scale yield m mg.,

$$s \text{ oz. per ton} = \frac{29.166m}{w}\Bigg)$$

Then $\dfrac{S(s - f)}{100}$ = correction to be added to the assay value per ton of fines to give total value per ton of original material

In case the metallics are poorer in gold than the fines, the expression $(s - f)$ will, of course, be negative, and the correction will be a deduction.

Sometimes, the iron or steel (from crushing and grinding machines) in a scale or concentrate is so plentiful as to necessitate removal by a magnet. In such a case, its weight should be taken into account, and it should either be rated as valueless, or it should be fluxed (or acid treated) and the contained precious metal prorated as above.

In the above expressions, the right-hand member (or the correction in 3) represents the value per ton of original due to scale; the left, the value due to fines. When the distributed value of the metallics is relatively large, say forming 5 per cent or more of the total, it is generally desirable to report the scale and fines separately on the basis of a ton of original. When duplicate or quadruplicate samples are taken and assayed as above, the scale value found is likely to differ materially owing to difficulties of sampling, while the different assays of fines may agree closely.

[1] Smoot, A. M., Trans., Can. Mining Inst., vol. XVII, p. 239; Mining Sci. Press, vol. CIX, p. 651, 1914.

[2] Liddell, D. M., *Eng. Mining Jour.*, vol. CI, p. 612, 1916.

If the total weight of scale in Method 2 is extremely small—for instance, when the scale consists merely of a few milligrams of gold from 10 a.t. of ore—the value w may become negligible, and the whole expression becomes simply

$$f + \frac{29.166m}{W}$$

or a small correction is to be added to f.

In calculations of this class for most metallurgical purposes, the error involved by the use of a good slide rule is usually less than those of the sampling and assay methods. But to avoid disputes in accounting, especially in the sale and purchase of ores and products, it is generally desirable to calculate more closely, and the use of a calculating machine is advisable.

Method 3*a*.—An ingenious variant of method 3, which obviates weighing the scale directly, has been used at Alaskan mines.[1] A definite number of assay tons (say 10 a.t.) is weighed out and passed over the sieve. The scale is made up to a definite fraction of an assay ton (say, 0.5 a.t.) by the addition of some of the fines; this 0.5 a.t. of mixture is then assayed, as well as the fines proper. Calling these assays s and f per ton, the difference gives the value to be multiplied by the percentage of mixed scale (which is always a simple number—in this case, 5 per cent) to give the correction which must be added to the fines assay.

The Assay of Ores Containing Their Chief Value in Free Gold. As already pointed out, these ores are difficult to get correct results from. Even though the free gold particles are very fine, it is impossible to distribute them throughout the bulk of the sample with absolute uniformity. The proper way to assay material of this kind is to take from 1,000 to 1,500 g. of the ore, crushed through a 100-mesh screen, place in a large Mason jar with a tight screw cover, mix to a rather thick pulp with water, and then add 3 to 4 cc. of mercury from a burette. It is essential that the mercury should be free from gold and silver, or its contents of precious metals known. Most mercury as purchased contains some gold. The jar and its contents are then agitated for 2 hours, best in some mechanical agitator. Then carefully separate the mercury from the ore by panning in a gold pan, saving all the pulp in another pan of somewhat larger size. None of the fine slimes of the ore must be permitted to escape. It may be necessary to add a little more mercury and a very little

[1] Cahill, W. E., Mining Sci. Press, vol. CX, p. 865, 1915

sodium amalgam during panning to collect any floured and sickened mercury. The pulp is allowed to settle in the pan, the surplus water carefully poured off, and the pan then set on a hot plate to dry. When dry, it is mixed on a cloth, and 1-a.t. samples taken and assayed by a proper method. The mercury is carefully transferred from the pan to a porcelain dish, washed with water to free from sands, dried with filter or blotting paper, and then transferred to a 20-g. crucible in which 20 g. of lead have been placed. To the crucible is then added a charge consisting of 30 g. PbO, 10 g. Na_2CO_3, 5 g. borax glass, and 0.5 g. argol and silver foil enough to part the gold.

The fusion is made by raising the heat very gradually; it is best to use a muffle that has not yet become red and has a good draft through it, to prevent the escape of mercury fumes into the room. The button from the fusion is cupelled in the usual manner. The gold is weighed in milligrams, and the weight divided by the grams of ore taken and multiplied by 29.166 gives the ounces gold per ton present as "free" gold. This figure added to the assay results from the pulp gives the total contents of the ore in ounces per ton.

Another method[1] is carried out as follows:

Take 6 a.t. of the sample crushed to pass 80 mesh, add sufficient water and a small amount of sulphuric acid to make a thin paste in an 8-in. porcelain mortar, add 8 g. of redistilled mercury, and grind thoroughly for 30 min. Then separate the tailings from the mercury by washing them off with a stream of water obtained, say, by attaching a hose to a hydrant. During the washing, the mortar should be given a rotary motion. Collect the overflow from the mortar in a large gold pan and treat the pannings as described in the method above. When the mercury in the mortar is quite clean from sands, give it a final wash with water, then dry it with filter paper and transfer to a crucible containing enough litharge with reducing agent to give a 20-g. button. Add enough silver to part the gold and start the fusion at a very low heat in the furnace. Cupel the lead button and weigh.

Divide the weight of the gold by the number of assay tons of ore taken and add this to the figure obtained from the assay of the pulp in order to get the total value of the ore in ounces per ton. When the ore to be assayed contains arsenopyrite and graphite,

[1] Roos, A. T., *Mining World*, vol. XXXII, p. 319.

some of these will adhere to the mercury. In order to overcome this difficulty, add to the washed mercury in the porcelain mortar 5 cc. of concentrated HNO_3 and enough silica to make a thin paste. Grind for a few minutes and then wash the silica and acid off with water and proceed as before.

Amalgamation Test to Determine the Amount of Free Gold Present.[1]—One hundred grams of crushed ore are weighed out into a citrate-of-magnesia bottle, 150 cc. of water added, and then 2 cc. of pure mercury from a burette. The stopper is clamped, the bottle rolled in a piece of cloth and placed in a moving shaker for 2 hours. It is then removed, opened, covered with the thumb, shaken, and inverted over a 3-in. porcelain dish, and as much clean mercury as possible allowed to run out. A little more water is added and more mercury allowed to run out into another dish, and so on as long as any comes out. If the mercury is not floured, nearly all is removed in two operations. All the clean mercury is then put into a 250-cc. beaker. The bottle is then shaken well and again inverted to let a little sand run out into a dish. This sand is then panned into an enameled dish, usually only a few globules of mercury being obtained. If much is found from this third inversion, the whole charge must be panned, and if the mercury is floured, a small globule of liquid sodium amalgam should be added to the pan. In ordinary routine work, the tailings from the panning are discarded. For special purposes, as when the tailings are to be tested by cyaniding, concentration, etc., they are allowed to settle completely, decanted, and, if necessary, dried for further tests or for assay. To the mercury after its collection in the 250-cc. beaker 0.5 g. of pure silver is added (if this has been carefully prepared and cleaned by treating in cyanide solution or weak nitric acid or by slightly amalgamating the surface, it may be used to pick up the small globules of mercury collected in panning); about 150 cc. of HNO_3, sp. gr. 1.14, previously warmed to about 70° C., is now poured into the beaker, which is set into an enameled pan on a hot plate and left there till all the mercury has dissolved. If not too hot, it is unnecessary to cover the beaker. As soon as the mercury disappears, the liquid is filtered on a 12.5-cm. paper previously wetted. The residue is rinsed onto the paper, washed once or twice with very diluted HNO_3 (not over 5 per cent) and once with water. Test lead is then sprinkled on the paper, it is

[1] Method used at the Homestake Mine, S. Dak. See *Trans.* A. I. M. E. vol. LII, p. 153.

folded, placed on test lead in a scorifier, and enough lead added to make a 20-g. button. Silver is added to insure parting and also a few grams of borax glass. The scorifier is then charged into the muffle, the paper burned, the charge scorified for a few minutes, poured, the button cupelled, and the bead parted and the gold weighed. From a 100-g. ore sample, each milligram of gold represents 0.29166 oz. or $6.03 free gold per ton.

Notes on the Carrying Out of the Amalgamation Test.—The amalgamation test is carried out for the purpose of determining the amount of precious metals that can be recovered from the ore in milling operations by means of amalgamation. The size of the crushed ore will influence the results; therefore, in different tests, the degree of fineness must be nearly constant. The exact fineness used depends upon conditions. Temperature has its influ-

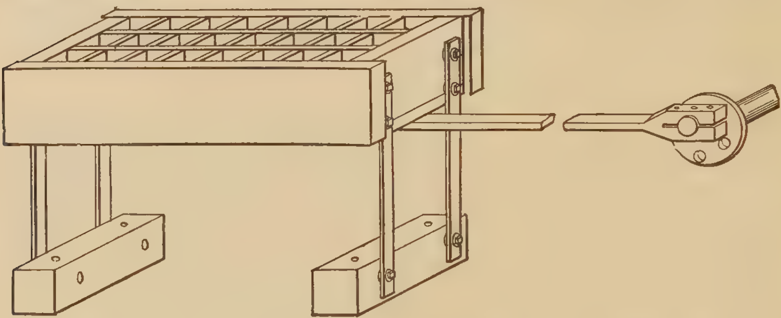

FIG. 55.—Homestake agitator for amalgamation and cyanide tests.

ence; if the tests are carried out at temperatures higher than the normal daily temperature, results will be higher. If the temperature be low, results will be lower. The addition of silver to the mercury reduces the time required for its solution by about one-half. Extreme care must be taken to get mercury and silver practically free from gold. It is desirable to run a blank assay on, say, 20 cc. of mercury and 5 g. of silver (representing ten times the quantity of each used in the assay). The mercury and silver are dissolved in acid, as stated in the amalgamation test, and the residues treated as described. The best mercury obtained after testing a number of new flasks and when used with commercial proof silver required a correction of 0.02 mg. of gold for 2 cc. mercury and 0.5 g. silver. The silver contained nearly half of the gold thus found. If the amount of silver in the ore recoverable by amalgamation is to be determined, the parting of the mercury by nitric acid must be replaced by the crucible

fusion of the mercury, as described in Method 1 for the assay of ores containing free gold.

Equipment Required for Routine Amalgamation Tests:

1. Shaking box with 24 compartments each 3 in. square and 6 in. deep, as shown in Fig. 55. The following are the details of construction: Sides and bottom made of 1.75-in. lumber; partitions of 0.5-in. lumber; sills 4 by 4-in. lumber; connecting rod 1¾ by ⅝-in. oak lumber, 4 ft. long; supports of light steel 1.5 by $\frac{5}{16}$ in. and 2 ft. long; shaft 1 in., 250 r.p.m.; throw of eccentric, 2 in. A frue vanner eccentric rod and supports may be used in the construction of the agitator. A pad should be placed at the bottom of each pocket. Pieces of canton flannel, 12 to 15 in. square, are used to wrap each magnesia bottle.

2. Twenty-four citrate-of-magnesia bottles with spring clamps and rubber washers. These have a capacity of 350 to 370 cc.

3. Twenty-four beakers, capacity about 250 cc.

4. Two enameled iron pans to hold 12 beakers each.

5. Six porcelain dishes, 3 in. in diameter, and two enameled iron pans, 8 in. in diameter and 2 in. deep.

6. Filtering rack for 12-2¾-in. funnels; 12 extra beakers.

7. Copper weighing scoop and copper funnel with steep sides for charging bottles.

8. Cylinder graduated to 100, 150, and 200 cc.

9. Glass-stoppered burette standing in enameled iron pan.

10. Supplies as mentioned in the assay.

The Assay of Cyanide Solutions. *Method* 1.[1]—Measure out any convenient volume into a beaker (preferably 10 or 20 a.t. using beakers of 500 to 700 cc. capacity). Add 10 to 20 cc. of lead-acetate solution containing 10 to 20 per cent of the salt, then introduce 3 to 4 g. of zinc dust in the form of an emulsion or suspension in water and stand on a hot plate. When moderately heated but before boiling, acidify with about 20 cc. strong hydrochloric acid, either c.p. or of the best commercial grade. Boil until action nearly ceases and the reduced lead has collected into a spongy mass. Filter on a "quick" paper, and wash precipitate twice with hydrant water. Remove the filter paper and precipitate and squeeze out as much water as possible. Place

[1] Due to Allan J. Clark, Homestake Mining Co. As solution samples are measured instead of being weighed, it must be remembered that the results refer to a *ton* by volume—ordinarily this the *fluid ton* on the volume occupied by 2000 lbs. water, which is commonly accepted as 32 cu. ft. in cyanide practice.

in a 2-in. scorifier with 10 to 15 g. of test lead and 3 to 5 g. of borax glass. Place at once in the muffle, burn the paper, scorify for only a few minutes, pour, cupel lead button, part, and weigh. Unless silver is to be determined, silver foil should be added to the scorifier for inquartation, or a measured volume of dilute $AgNO_3$ solution may be added to the beakers from a burette.

Notes on the Method.—About 100 g. zinc dust are usually mixed with 300 cc. of water in a bottle with an 1/8-in. glass tube passing through the cork. This mixture is shaken into a capsule of the proper size used as a measure. The other reagents must be roughly measured. Their proportions should be varied slightly until conditions are found which yield a "sponge" of lead quickly with the particular solutions regularly assayed. Impure hydrochloric acid does not give good results, nor do other acids. It is essential that nearly all the zinc be dissolved before filtering. Comparatively cheap filter papers answer well. If a 300-cc. flask be regraduated to deliver 301.45 cc., every milligram of gold obtained from this volume represents $2 gold value per ton. If copper is present in solutions, a somewhat longer scorification than above stated may be desirable.

This procedure was suggested by Chiddey's method[1] in which zinc shavings and lead salt are used to produce a lead sponge. In this original method, the lead sponge is recovered by hand and not filtered and then cupelled direct without a preliminary scorification.

Clark's method gives somewhat better results on low-grade solutions than evaporation with litharge or litharge-bearing flux. It has the particular advantage of being exceedingly rapid as compared with the tedious evaporation methods.

Method 2. *Evaporation Method.*—Measure out 5 to 10 a. t. or more of solution by means of a properly graduated flask and transfer to either porcelain- or agate-ware evaporating dishes, of 300 to 500 cc. capacity. To the solution add 50 to 60 g. of litharge and place the dishes in a sand bath on a hot plate and carefully evaporate to almost complete dryness. If agate-ware dishes are used, it is essential that the agate lining be unbroken; otherwise, precious metals will precipitate on the iron surface and adhere to the same, giving low results in the assay. Tin dishes should not be used. When practically dry, transfer contents by

[1] Chiddey, A., *Eng. Mining Jour.*, vol. LXXV, p. 473. Consult, also, Barton, W. H., *Western Chem. Met.*, vol. IV, p. 67, and Whitby A., *Jour. Chem. Met Mining Soc. S. Africa*, vol., X, pp. 134, 211, 288.

means of a spatula to a glazed paper and remove any adhering litharge from the dish by means of a moist piece of filter paper, thoroughly wiping out the dish. If the evaporation has not been carried too far, this can readily be done. Then mix in a 20-g. crucible 25 g. litharge, 15 g. Na_2CO_3, 2 g. argol, 2 g. SiO_2, and 5 g. borax glass, and transfer the litharge from the evaporation and filter paper to the crucible and again mix with a spatula. Fuse the charge and proceed as usual. Unless silver is to be determined, add silver foil to the crucible before fusion.

Evaporation methods conducted in dishes made of lead foil have the disadvantage of permitting the use of comparatively small quantities of solution only and very frequently give low results.

Assay of Cyanide Solutions for Gold (and Silver). *Copper Sulphate Method as Used in South Africa.*—This is a rapid method which does not require heat.

REAGENTS

1. Sodium cyanide	Saturated solution
2. Copper sulphate	30 per cent
3. Sodium sulphite	20 per cent
4. Sulphuric acid	40 per cent
5. Potassium ferrocyanide	4 per cent

The solution should be alkaline. Measure out 5 to 20 a.t. into a large beaker or conical flask, add about 1 cc. of sodium cyanide solution, and then 10 cc. of each of the others in the order given, stirring after each addition. Leave for ½ hour, when sulphur dioxide should be evolved freely. Filter through a rapid paper previously wetted. When thoroughly drained, place about 1-a.t. solution flux in a small (12 or 15 g.) crucible, add the drained filter paper, and sprinkle with flux—about ½ a.t. If gold only is to be determined, add a suitable piece of silver or enough standard silver solution (1 cc. = 10 mg. Ag) for parting. Fuse, cupel, etc.

FLUX

	Grams
Sodium carbonate	5
Litharge	20 to 25
Silica	6
Borax glass	3 to 5

Reducing agent depending on solution, to give 20 g. lead.

In place of reagents 2, 3, 4, 10 cc. of a saturated *colorless* solution of cuprous chloride may be used; this is prepared by keeping a large excess of copper sulphate and copper wire or foil in contact with strong commercial hydrochloric acid in a stoppered bottle.

If much lime is present in solutions, it is better to substitute concentrated hydrochloric acid for the sulphuric in the sulphate method, as calcium sulphate tends to slow filtration.[1]

The Assay of Slags and Cupels for the Correction Assay. *a. Slags.*—The charge for these depends upon whether they are acid or basic. Particular care must be taken to get a charge that will completely decompose the original slag. If this is acid, the charge should aim to make a new slag more basic, and *vice versa.* The lead button should be from 25 to 30 g. in weight. Many assayers frequently add simply litharge and reducing agent to the slag in making the fusion. This is not always desirable, for if the slag already has much litharge in it, soda, etc., may with profit be added as the extra base in place of litharge.

b. Cupels.—The bone ash of the cupel will not unite with fluxes to form slags but remains suspended in the fusion. For this reason, the cupel should be put through a 150- to 200-mesh screen before assaying, the litharge-stained portion only being taken. For one large cupel, or two small ones, the charge is as follows:

Cupel		Borax glass	45 g.
PbO	60 g.	Argol	2.5 g.
Na_2CO_3	25 g.	Soda cover	

Fluor spar is not desirable in the assay of cupels, as it merely adds another ingredient in suspension.

Magnesia cupels may be fluxed with the following charge:

Cupel		Borax glass	20 g.
PbO	40 g.	Silica	10 g.
Na_2CO_3	20 g.	Argol	2.5 g.
	Borax cover		

Cement cupels are more easily fluxed, and an ordinary crucible charge for a somewhat basic ore will answer very well.

It is economical to mix the slag and cupel for fusion, after grinding each separately, when the total correction is desired.

[1] See "Rand Assay Practice."

The Assay of Material Containing Metallic Iron.—Material of this kind will be obtained in the clean-up of mortar boxes of stamp mills, the iron being present as pellets, and much larger pieces mixed with sand, pebbles, etc. It cannot be crushed and is assayed in the state received. Its correct sampling is practically impossible. Most of the iron may be removed by solution in somewhat diluted hydrochloric acid. The residue is then filtered off, washed, and the filter and contents burned in a crucible and fluxed. If very small in quantity, it may be treated in a scorifier with test lead and a little borax.

CHAPTER XII

ERRORS IN THE ASSAY FOR GOLD AND SILVER

Losses in the Cupellation of Pure Gold and Silver.—These losses may be divided into (1) losses by absorption; (2) losses by volatilization. The losses of gold and silver in the cupellation are functions of (*a*) the temperature of cupellation; (*b*) the amount of lead with which the gold and silver is cupelled; (*c*) the physical nature of the cupel; (*d*) the nature and amount of impurities present; (*e*) the influence which silver has on the gold loss, and *vice versa*.

There is considerable literature extant upon losses in cupellation of the two precious metals, but in the older researches the temperature influence is but vaguely defined, owing to the lack of means for ready and satisfactory temperature measurements, a deficiency which is now supplied by the Le Chatelier platinum-rhodium pyrometer. Losses are also expressed as percentages of the total amount of metal cupelled, and then the average percentage losses are indicated. That this is very deceptive is made evident by reference to the curve of losses accompanying this chapter. (Fig. 56).

It is for this reason that the statement of results given by Mason and Bowman,[1] that the average loss in cupellation of pure silver under normal conditions is 1.99 per cent and for gold 0.296 per cent, does not convey any very definite idea, unless the amount of metal cupelled is accurately specified, as well as the temperature. This fact has been noted by other observers,[2] but no effort has been made to express results coordinately.

The following data show the losses which occur:

[1] *Jour. Am. Chem. Soc.*, vol. XVI, p. 505.

[2] Kaufman, *Eng. Mining Jour.*, vol. LXXIII, p. 829; Miller and Fulton, "*School Mines Quart.*," vol. XVII, p. 169.

TABLE XXXVIII.—CUPELLATION OF PURE SILVER
J. Eager and W. Welch[1]

Amount of silver, milligrams	Amount of lead, grams	Temperature, degrees centigrade[2]	Total loss, per cent
204.62	10	700	1.02 (average)
205	10	775	1.28
203	10	850	1.73
203	10	925	3.65
203	10	1,000	4.87

[1] LODGE, "Notes on Assaying," p. 59.
[2] Of air in muffle, directly above cupel.

TABLE XXXIX.—CUPELLATION OF PURE SILVER
L. D. Godshall[1]
Approximate Temperature of Air in Muffle = 750° C.

Amount of silver, milligrams	Amount of lead, grams	Total loss, per cent	Average loss, per cent
2	7.5	3.66	4.885
2	15.0	4.40	
2	22.5	5.52	
2	30.0	5.96	
5	7.5	3.29	3.515
5	15.0	2.63	
5	22.5	3.83	
5	30.0	4.31	
10	7.5	3.73	3.84
10	15.0	2.89	
10	22.5	4.47	
10	30.0	4.26	
20	7.5	3.42	3.11
20	15.0	2.34	
20	22.5	3.59	
20	30.0	3.10	
50	7.5	2.14	2.45
50	15.0	2.46	
50	22.5	2.33	
50	30.0	2.89	
100	7.5	2.11	2.22
100	15.0	2.40	
100	22.5	2.10	
100	30.0	2.28	
200	7.5	1.71	1.76
200	15.0	1.64	
200	22.5	1.62	
200	30.0	2.07	

[1] *Trans.* A. I. M. E., vol. XXVI, p. 473.

TABLE XL.—CUPELLATION OF PURE SILVER

Kaufman[1]

Approximate Temperature of Air in Muffle = 750° C.

Amount of silver, milligrams	Amount of lead, grams	Total loss, per cent	Average loss, per cent
25	5	2.14	
25	10	2.63 (2 38, 2.43)	2.39
25	15	2.69	
25	25	2.09 (2.48, 2.44)	
50	5	1.43	
50	10	2.23 (2.10, 1.96)	2.00
50	15	2.14	
50	25	1.86 (2.25, 2.37)	
100	5	1.30	
100	10	1.61 (1.82, 1.42)	1.68
100	15	1.68	
100	25	2.12 (1.93, 2.12)	
200	5	0.86	
200	10	1.24 (1.29, 1.17)	1.31
200	15	1.40	
200	25	1.74 (1.46, 1.76)	

[1] *Eng. Mining Journal*, vol. LXXIII, p. 829.

Parentheses indicate different types of cupels, *viz.*, bone ash made up, respectively, with pearl ash and stale beer. The main figures were obtained by bone-ash cupels made up with water. The results, viewed as a whole, indicate that all three types have equal merit. Godshall (Table XXXIX) experimented with different types of standard bone-ash cupels (some made at the mint), with the same result.

The agreement amongst the different writers is very close, when the fact is taken into consideration that in the last two

Authority	Amount of silver, milligrams	Amount of lead, grams	Temperature, degrees centigrade, of air in muffle	Total loss, per cent
Eager and Welch	205	10	775	1.28
Godshall	200	7.5	?(feathers)	1.71
Kaufman	200	10	?(feathers)	1.24
Liddell[1]	102	20	?(feathers)	1.70

[1] *Eng. Mining Jour.*, vol. LXXXIX, p. 1264.

cases no precise statement concerning temperature is made and that the amounts of lead differ somewhat. Very detailed data on cupellation losses of silver, taking into account different kind of cupels, size of cupel material, and temperature, made by H. T. Mann and C. Y. Clayton, confirm the correctness of earlier work.[1]

The accompanying curves are constructed from figures in Godshall's paper. The general averages are taken, and while his losses are, perhaps, a trifle higher than the best work calls for at the present day (owing to a better recognition of the precise temperature required), they form the best and most complete data for the construction of curves showing the relation between amounts of silver cupelled and the percentage loss. An equation covering the case is given in Fig. 56.[2]

The influence of the size of lead button is clearly discernible by the ordinates of the curves. The temperature variations will show in the same way.

The literature of gold losses is considerably less than that for silver. Rose[3] discusses them in the gold-bullion assay. He gives the total loss on bullion 916.6 fine, under normal temperature conditions, as from 0.4 to 0.8 per 1,000, of which 82 per cent is cupel absorption, 10 per cent volatilization (probably), and 8 per cent solution in acid. This, calculated to percentage on actual gold, is equivalent to 0.0803 per cent for the highest loss. (This is cupel loss only, not including solution loss.)

Hillebrand and Allen's results contain interesting data regarding the relative losses by absorption and volatilization, to which reference will be made again.

A Rule Governing Cupellation Losses.[4]—The results of an immense number of experiments have been published at various times during the past hundred years giving the actual or the percentage losses suffered under various conditions of cupellation, but the data are widely scattered and few attempts have been made to correlate them, so that no definite law has heretofore been shown to exist governing the relation of weight and loss. If such a law were known, it would enable a correction to be applied to a button of any weight, by a calculation applied to the loss observed in a proof of an entirely different weight but cupelled

[1] Mo. School Mines, *Tech. Bull.* 3, vol. 2, 1916.

[2] Van Nuys, C. C., Private communication.

[3] "Metallurgy of Gold," p. 506, 1902.

[4] Sharwood, W. J., *Trans.* A. I. M. E., vol. LII, p. 179, 1915.

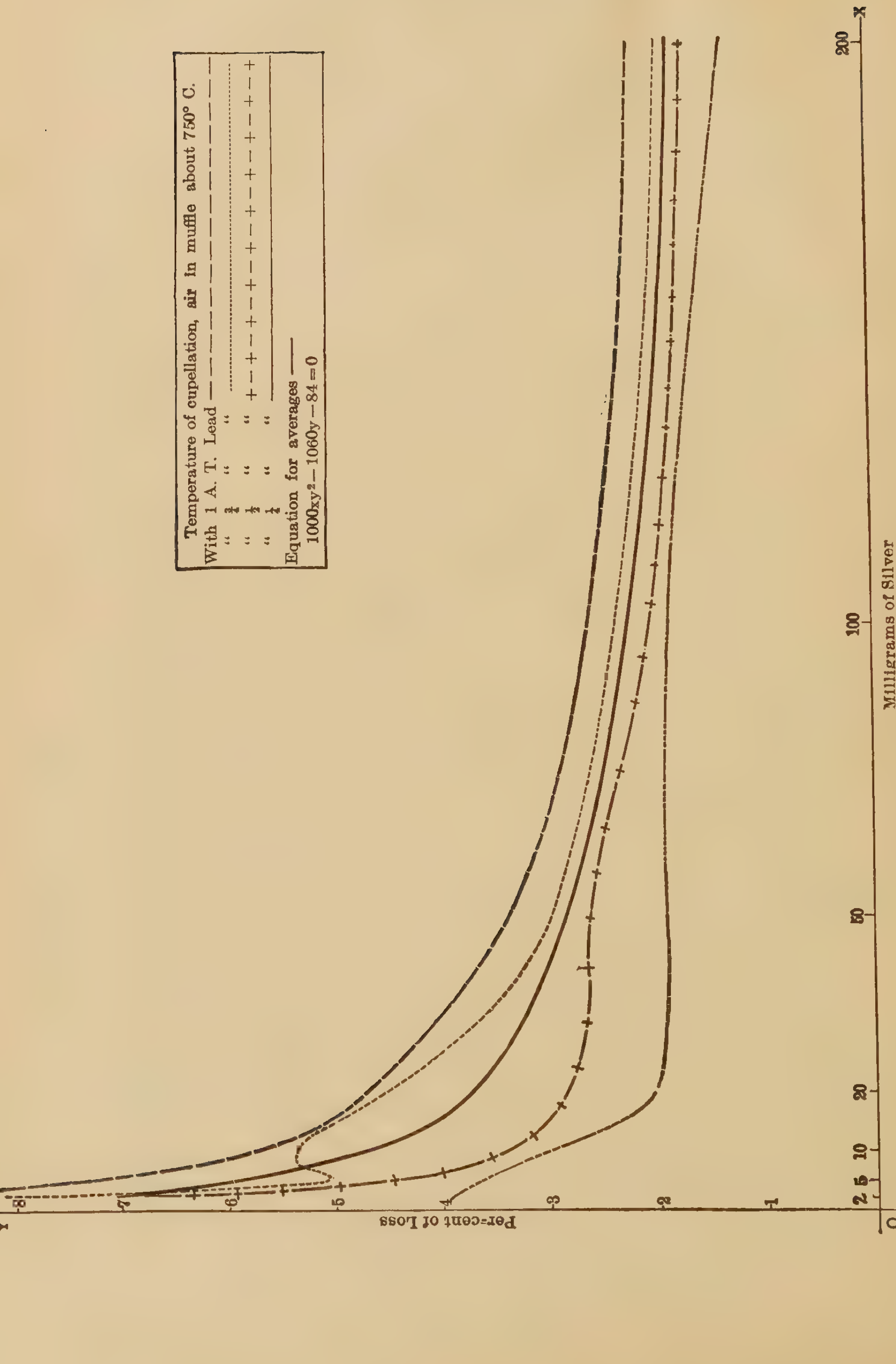

FIG. 56.—Curve showing silver losses in cupellation.

at the same time under the same conditions. It is believed that such a rule is now available.

This empiric rule may be thus enunciated: *When a given amount of silver (or gold) is cupelled with a given amount of lead, under a fixed set of conditions as to temperature, etc., the apparent loss of weight sustained by the precious metal is directly proportional to the surface of the button of fine metal remaining.*

Probably, the calculation should be based on the original weight of precious metal taken, but in practice we have to depend

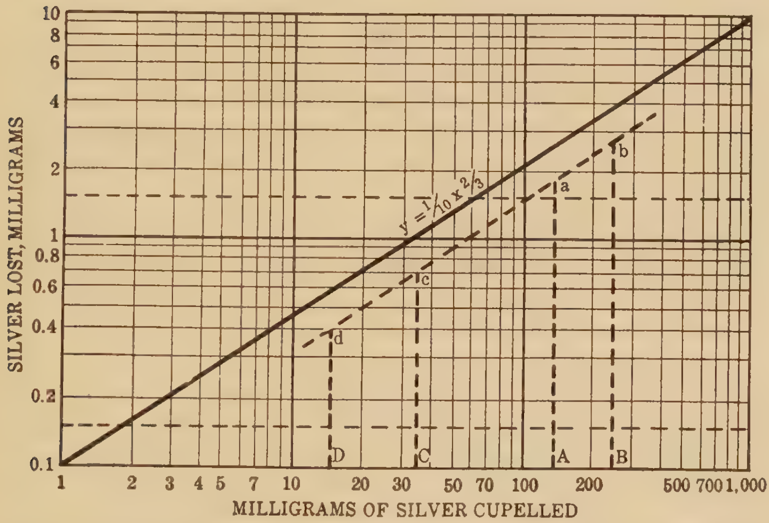

FIG. 57.—Curve representing silver losses in cupellation plotted on logarithmic cross-section paper.

on the weight remaining. Variations in the amount of lead have comparatively little influence, and temperature conditions in a given row across a muffle are nearly uniform, so that for practical purposes the proportionality holds good for any one row in a cupellation run, provided the amounts of lead do not differ extremely. Most other variations have smaller effects. If the above is true, the following must also be true:

The loss of weight varies as the two-thirds power of the weight or as the square of the diameter of the button.

The percentage loss varies inversely as the diameter of the button or inversely as the cube root of the weight.

Examination of a large number of experimental results as well as the published data of others proves that the last proposition is a close approximation of the truth and, therefore, proves the others.

As to the possible application of this rule: An approximate correction may be obtained for an ore or the like, if one proof, as near the expected weight as possible, is cupelled in each row, and its exact loss noted. The corresponding point is plotted on the diagram (*a* in Fig. 57, *A* representing the final weight), and a straightedge is placed on the diagram, or a line drawn through *a*, parallel to the guide line $y = x^{2/3}$. Noting the points on the line or straightedge corresponding to the weights *B*, *C*, *D* of other buttons weighed, the correction for each is read at once from the scale. In the example plotted in Fig. 57, a button of 140 mg. weight has lost 1.8 mg.; from this it appears that other buttons of 250, 35, and 15 mg. will, respectively, have lost about 2.85, 0.72, and 0.40 mg.

Cupellation of Gold-silver Alloys.—The loss of gold and silver in cupellation is somewhat different when both gold and silver are present from the loss when either metal alone is present.

Table XLI.—Cupellation of Gold

Eager and Welch[1]

Amount of gold	Amount of lead	Temperature, degrees centigrade[2]	Total loss, per cent
201 mg.	10 g.	775	0.155
201	10	850	0.430
204	10	925	0.460
201	10	1000	1.430
201	10	1075	3.000

[1] Lodge, "Notes on Assaying," p. 142.

[2] Of air in muffle, directly above cupel.

Rose shows (Table XLIII) the protective action that silver exercises over gold, the total loss of gold decreasing as the amount of silver present increases. Hillebrand and Allen show how the total loss is distributed between absorption by the cupel and volatilization. It is evident that while the total loss of gold is decreased by the presence of silver, the volatilization loss of gold is increased by the presence of silver (compare tables XLII and

XLIV). When gold and silver are present in the ratio of 1:2, their averages are as follows:

Of the total gold loss, 68 per cent is absorbed, 32 per cent is volatilized.

Of the total silver loss, 71 per cent is absorbed, 29 per cent is volatilized.

TABLE XLII.—CUPELLATION OF GOLD
Hillebrand and Allen[1]

Amount of gold, milligrams	Amount of lead, grams	Approximate temperature, degrees centigrade, of air in muffle	Total loss, per cent	Total loss, cupel absorption, per cent	Total loss volatilized, per cent
30.58	25	750 (feathers)	0.36		
30.32	25	Increased	1.19	80	20
30.63	25	Increased	1.76		
30.45	25	Increased	3.78	77	23
30.16	25	Increased	4.17	93	7
30.66	25	Back of muffle	4.43	92	8
10.34	25	750 (front of muffle)	0.29		
10.25	25	Increased	4.68		
10.29	25	Increased	1.36		
10.27	25	Increased	10.42		
10.17	25	Back of muffle	16.43		

[1] U. S. Geol. Survey. *Bull.* 253.

TABLE XLIII.—CUPELLATION OF GOLD WITH SILVER
Rose[1]

Amount of gold, milligrams	Amount of silver, milligrams	Amount of lead, grams	Temperature of cupellation, degrees centigrade, of air in muffle	Total loss gold, per cent
1	4	25	900	1.2
1	6	25	900	1.05
1	8	10	900	0.90
1	10	25	900	0.80
1	6	25	700	0.45
1	10	25	700	0.39
500	1,250	10	900	0.055

[1] *Eng. Mining Journal*, vol. LXXIX, p. 708. Results, probably too high on account of high temperatures.

As the total loss is determined, however, by the difference in weight between the proof gold and silver and the weights of the cupelled bead and parted gold, and the volatilization item by the difference between the total loss and the amount recovered by the reassay of the cupel, it is evident that certain errors obtain which apparently make the volatilization loss appear greater

TABLE XLIV.—CUPELLATION OF GOLD-SILVER ALLOYS

Hillebrand and Allen

All Cupellations Made with 25 G. Lead

Amount of gold, milligrams	Amount of silver, milligrams	Temperature, degrees centigrade	Total loss, per cent		Absorbed by cupel, per cent		Volatilized, per cent	
			Gold	Silver	Gold	Silver	Gold	Silver
30.06	90.51	750 (air in muffle)	0.50	1.70				
30.40	90.19	Increased..	1.22	3.73				
30.60	90.74	Increased..	2.32	5.51				
30.07	90.67	Increased..	3.76	7.66				
30.61	90.75	Back of muffle	3.89	7.98				
15.56	45.06	Front, 750.	0.19	1.91	67	81	33	19
15.14	45.19	Increased..	0.40	3.30	83	78	17	22
15.15	45.41	Increased..	1.52	4.14	52	63	48	37
15.44	45.30	Increased..	2.07	5.78	67	62	33	38
15.52	45.59	Increased..	2.59	6.55	67	70	33	30
15.39	45.05	Back of muffle	2.40	6.61	73	71	27	29
10.67	30.33	Front, 750	0.47	2.17				
10.57	30.64	Increased..	1.61	5.68				
10.53	30.42	Increased..	5.13	10.19				
10.63	30.52	Increased..	10.63	15.99				
10.60	30.38	Increased..	12.46	18.34				
10.21	30.44	Back of muffle	12.53	18.69				

than it really is. The error, however, cannot be very great. The data are inconclusive regarding the influence of the temperature on the relative losses by absorption and volatilization, but it seems indicated that the volatilization loss is proportionately greater with an increase of the temperature of cupellation.

Losses in the Assay of Ores.—Table XLV, etc., show losses of gold and silver in the assay of ores, during fusion and cupellation, as influenced by the presence of certain impurities.

TABLE XLV.—TELLURIDE ORES

Crucible Fusion

Milligrams of gold in weight of ore taken for assay	Grams of lead button	Slag loss, per cent	Cupel absorption, per cent
493.83[1]	20	0.51	1.56[7]
95.57	20	0.38	0.23[5]
1.54	20	1.30	0.40
1.95	20	0.50	0.50
1.19	20	....	0.40
1.17	20	....	0.40
3.60	20	2.14	0.80
6.20	20	0.64	0.32
6.23	20	0.50	0.64
1.38	20	0.80	1.00
18.18[2]	25	0.49	
5.85	25	1.03	0.12[6]
34.0[3]	27	0.21	0.23
34.0	27	0.56	
34.0	25	0.15	0.41
68.0	25	0.13	0.07
68.0	25	0.16	0.22
15.5[4]	..	0.25	0.19[8]
15.49	..	0.13	0.38
19.54	..	0.20	0.23
19.63	..	0.10	0.25

[1] WOODWARD, *Western Chem. Met.*, vol. I, p. 12.
[2] FULTON, in *School Mines Quart.*, vol. XIX, p. 419.
[3] LODGE, *Tech. Quart.*, vol. XII, p. 171 (averages) 1899.
[4] U. S. Geol. Survey *Bull.* 253 (averages; Hillebrand and Allen).
[5] Average of 34 fusions, tellurium in all beads.
[6] Average of 10 fusions.
[7] Cripple Creek flux.
[8] Excess litharge charge.

Table XLVII indicates the range of corrections found in a number of normal melts made in assaying rich cyanide precipitate. Occasionally, owing to the occurrence of small shots of lead in the slag, the slag loss in one melt may rise to 1 per cent or more. In general practice, the slag and cupel are melted together, and the mixed correction doré button thus obtained is weighed with the main doré button. The main button and cor-

rection are then inquarted together by cupelling with the proper weight of silver, as estimated from a comparison of the color of

TABLE XLVI.—ZINCIFEROUS MATERIAL, ETC.

Milligrams of Au and Ag in weight of ore taken for assay		Weight of lead button, grams	Method of assay	Slag loss, per cent		Cupel absorption, per cent		Remarks
Au	Ag			Au	Ag	Au	Ag	
232.0[1]	287.0	18	Scorification after acid treatment	0.06	0.40	0.11	1.30	Zn ppt. containing 42.3 per cent Zn
232.0	284.0	18	Scorification after acid treatment	0.04	0.34	0.08	1.10	Figures represent averages
232.0	284.0	18	Direct crucible fusion	1.04	1.10	0.16	1.50	
233.0[2]	197.0	20	Crucible fusion after acid treatment	0.06	0.51	0.18	1.18	Zn ppt. containing 14.3 per cent Zn, 9.1 per cent Cu.
233.0	202.0	20	Direct crucible fusion	0.15	2.73	0.16	1.29	Figures represent averages
[3]	561.0	20	Crucible fusion niter method	....	0.75	....	1.38	Galena
	567.0	20	Crucible fusion niter method	....	0.65	....	1.42	Galena
[3]	175.0	20	Crucible fusion niter method	....	0.23	....	1.90	Siliceous ore containing some copper
	174.0	20		....	0.37	....	1.66	Siliceous ore containing some copper

[1] FULTON and CRAWFORD, *School Mines Quart.*, vol. XXII, p. 153.
[2] LODGE, *Trans.* A. I. M. E., vol. XXXIV, p. 432.
[3] MILLER, *School Mines Quart.*, vol. XIX, p. 43.

TABLE XLVII.—ZINC PRECIPITATE FROM CYANIDE SOLUTIONS; ASSAYED BY CRUCIBLE FUSION, USING 0.05 A. T.

Milligrams precious metal in fusion		Grams lead button	Percentage loss in slag		Percentage loss in cupel	
Gold	Silver		Gold	Silver	Gold	Silver
390	137	24	0.1	0.15 to 0.2	0.6 to 0.8	2.5 to 3.0
300 to 330	100 to 110	25	0.08 to 0.12	0.21 to 0.26	0.2	1.2 to 1.5
110	38	25	0.16 to 0.20	0.45 to 0.50	0.25 to 0.28	2.1 to 2.3

the main doré button with a series of "touch needles" of gold and silver ranging from 500 to 950 gold fineness.

TABLE XLVIII.[1]—HIGH-GRADE CARBONATE AND SULPHIDE-SILVER ORES[2]

Amount of Au and Ag in weight of ore taken for assay		Weight of lead button, grams	Method of assay	Slag loss, per cent		Cupel absorption, per cent		Second correction from fusion of slags and cupels of first correction, per cent
Au, milligrams	Ag, milligrams			Au	Ag	Au	Ag	
	1,130	24	Crucible fusion.....	....	0.76	....	1.25	0.248
	1,130	28	Crucible fusion.....	....	0.361	....	0.956	
	1,130	28	Crucible fusion Double amount of fluxes	....	0.511	....	0.88	0.15
	1,130	32	Crucible fusion Double amount of fluxes	....	0.736	....	1.02	0.15
	226	15	Scorification.......	....	2.8	....	1.40	0.559
24	1,719	25	Crucible fusion.....	0.05	0.143	0.07	0.711	
12	860	20	Scorification.......	0.12	0.72	0.08	0.86	

[1] First five results on lead-carbonate ore, last two on silver sulphides. All results represent averages.

[2] MILLER and FULTON, *ibid.*, vol. XVII, p. 160.

TABLE XLIX.—CUPRIFEROUS MATERIAL

Amount of Au and Ag in weight of ore taken for assay		Weight of lead button, grams	Method of assay	Total loss recovered including slag and cupel, per cent		Remarks
Au, milligrams	Ag, milligrams			Au	Ag	
11.46	88.0	20	Crucible fusion	0.96	2.90	Mattes containing about 20 per cent Cu
5.36	46.8	20	Crucible fusion	2.98	4.30	
4.20	37.24	20	Crucible fusion	2.38	2.70	
3.52	33.79	20	Crucible fusion	2.84	5.47	
4.20	37.24	20	Scorification	5.95	5.26	
3.52	33.79	20	Scorification	3.12	5.71	

The foregoing tables represent, for the most part, averages and, in every case, the losses for the normal assay; *i.e.*, in the case of the fusion, the charge known to yield the best results and the proper temperature for cupellation. The losses are, therefore, to be ascribed to the nature of the material assayed, chiefly to the influence of certain elements present. In considering the percentage of loss, it must be recalled that this varies inversely with the amount of precious metal in the charge, *i.e.*, with the size of the gold-silver bead. The sum of the cupel absorption and the slag loss (which can, in part, be recovered) is not the total loss, as it does not include that by volatilization, which is small in most cases but, in some cases, again, may be quite appreciable, as in the case of telluride ores. What the loss is in slag, when no element like tellurium, copper, zinc, etc., is present, may be seen by reference to Table XLVI, to those assays fused after acid treatment, and to Table XLVIII, showing crucible fusions on lead-carbonate ore. The slag loss in gold and silver for these ores is very small. In cases where the impurity present and causing loss is nearly all eliminated in the fusion, *e.g.*, zinc, antimony, etc., the cupel absorption is practically that for pure silver and gold under the same circumstances. Where the impurity is tellurium, or selenium, or copper, the cupel absorption is decidedly increased. One fact is to be noted: that the slag losses present no regularity, even for the same material. This is probably due partly to differences of slag composition among different experimenters, partly to difference of temperature of fusion, and also to the method of refusion of slag.

The high loss in scorification slags shown in Table XLVIII for lead-carbonate ores containing silver is due to the general unsuitability of the ore for scorification, although scorification slags show higher losses than crucible slags. That, in spite of this, scorification assays on silver-bearing material show equally good and, in many cases, better results than the crucible assay is due to the fact that the silver beads retain small quantities of lead and copper (see farther on) and to the fact that in the multiplication of the weight of the silver bead by 5 or 10, or whatever the assay-ton factor may be, this error is multiplied, giving an apparently better result.

The amount of slag has comparatively little influence on the amount of precious metals retained, provided the amount of collecting lead is ample. Buttons of less than 18 to 20 g. should

not be made, and if the amount of slag is great or the quantity of silver and gold in the charge is more than 500 mg., 25- and 30-g. buttons are essential. In the case of large buttons which contain no impurity, it is also best to cupel direct, if possible, rather than rescorify to smaller size, as the rescorification causes greater loss than the direct cupellations.

During scorification there is also an appreciable loss of the precious metals by volatilization, which is absent in the crucible assay. This, in the case of telluride or zinciferous ores, may become so great as to put scorification out of the question.

Other Errors. *Retention of Lead in Cupelled Beads.*—Small quantities of lead are almost invariably retained in the gold and silver beads with ordinary temperatures of cupellation. Hillebrand and Allen,[1] in two careful experiments on sets of three beads, approximately together 90 mg. gold, found that 0.30 and 0.37 per cent, respectively, of lead were retained. This retention of lead cannot be corrected by leaving the bead in the muffle for some length of time after the blick, as this is, of course, prohibitive in the case of silver and, in the case of gold, seems actually to cause an increase of weight. It has already been stated that copper and tellurium are very apt to be present in the final bead, when they occur in the ore in appreciable quantity and bismuth also tends to remain with the gold and silver. The retention of base metal by the bead causes a plus error in silver but will not affect the result on gold unless the parting is by H_2SO_4; and where the weight of the bead is multiplied by a factor to get results per ton, the final error in silver may be very appreciable. The presence of copper in the final bead practically insures the complete removal of the lead.

In order to define the term *fine silver*, the following analysis of government fine silver is appended.

Ag, 99.929 per cent; Cu, 0.056 per cent; Pb, 0.003 per cent; Au, 0.007 per cent; As, 0.001 per cent; Sb, 0.002 per cent; Fe, 0.001 per cent; Zn trace.[2]

Retention of Silver by the Parted Gold.—Ordinary parted gold, after the proper treatment with weak and strong acid, retains from 0.05 to 0.10 per cent of silver. In the assay of gold bullion after the first acid treatment of the quartation alloy, the gold, on the average, retains 0.25 per cent silver. After the second

[1] U. S. Geol. Survey *Bull.* 253.

[2] *Mineral Ind.*, vol. XV, p. 545.

acid treatment, the final silver retention is from 0.06 to 0.09 per cent, depending on the time of boiling. If the amount of silver to gold in the quartation alloy is less than 2.5 to 1, somewhat more than the above amount of silver will be retained.[1]

Silver can, practically, be completely extracted by more than two treatments with acids, according to Hillebrand and Allen.[2] In the ordinary assay for ores, as usually carried out, it is safe to assume that some silver is invariably retained by the gold, and frequently much more than is supposed; however, with low-grade ores, this retention is negligible.

Solution of Gold by Acid.—It is essential that the nitric acid used for parting be free from impurities, especially from hydrochloric acid and chlorine; otherwise, more or less aqua regia may be formed and solution of gold is sure to follow. Gold is quite soluble in mixtures of hot sulphuric and nitric acid[3] and is again precipitated by dilution.

According to Hillebrand and Allen,[4] nitrous acid (HNO_2) and mixtures of HNO_3 and HNO_2 do not dissolve gold, though there is much earlier literature to the contrary. Nitrous acid has frequently been considered in this connection, as it is formed, to some extent, by the action of HNO_3 on silver.

According to Rose,[5] some gold is dissolved by nitric acid on continued boiling to constant gravity of acid. This solution is placed in the bullion assay at 0.05 per cent or 0.5 parts per 1,000. Hillebrand and Allen state that the loss of gold by solution is very small and irregular. It may be disregarded in the ore assay, where the time of contact is seldom long. The solubility of gold in HNO_3 is readily demonstrated when large quantities of gold are used. F. P. Dewey,[6] in careful experiments, showed the solution of gold to the extent of 660 mg. per liter of concentrated acid, on boiling about 25 g. gold for 2 hours. He states that the temperature (120° C.) required to boil concentrated acid has an influence as decided as the strength of the acid.

Occluded Gases.—Parted gold beads and "cornets" retain about twice their volume in occluded gases after annealing. The principal gas is stated to be carbon monoxide. Two volumes

[1] Rose, "Metallurgy of Gold," p. 453.

[2] U. S. Geol. Survey, *Bull.* 253.

[3] Lenher, *Jour. Am. Chem. Soc.*, vol. XXVI, p. 552.

[4] *Ibid.*

[5] *Ibid.*, p. 507.

[6] *Jour. Am. Chem. Soc.*, vol. XXXII, p. 318.

amount to 0.02 per cent by weight, which is already allowed for in the silver retention.

Errors in Weighing.—The best scales are accurate to 0.01 mg., and scales can be obtained weighing to 0.005 mg. This last is used in assay offices, where great accuracy is required, on such material as bullions, rich mattes, etc. It is usually an unnecessary refinement in the ordinary ore assay, for the reason that the probable error in the assay is greater than this.

The errors in the assay for gold and silver may be summarized as follows:

1. Losses by absorption or solution in the slag of the fusion.
2. Losses by volatilization during fusion.
3. Losses by absorption during cupellation.
4. Losses by volatilization during cupellation.
5. Errors by gain in weight of bead, due to retention of foreign elements. These affect results on silver chiefly.
6. Errors in weight of gold after parting by the retention of silver and occluded gases and minute amounts of base metals.
7. Losses of gold by solution in nitric acid.
8. Errors in weighing.

The chief losses are 1 and 3, which can be recovered by "corrected assay," *i.e.*, by reassay of slag and cupel, to the extent of about 80 to 85 per cent. Wherever the highest accuracy is required, corrected assays should always be made. The losses by volatilization are usually slight, although from the foregoing data these are sometimes seen to be considerable. The retention of foreign metals by the bead is a plus error in favor of silver, and the retention of silver in the parted gold is a plus error in favor of gold. Silver losses are considerably greater in magnitude than gold losses. The total amount of precious metal recovered by the assay varies with the nature of the material. Designating the total amount of gold and silver in an ore or product as 100, the corrected assay will show from 99 to 99.8 per cent of the gold and from 98 to 100+ per cent of the silver, the high silver result, in some cases, being due to retention of foreign metal.

In the bullion assay for gold, the algebraic sum of the errors outlined, the losses being designated minus and the gains plus, is called the *surcharge*. In the gold-bullion assay, this will usually vary from +0.25 per 1,000 in very pure gold bullion to −2.5 per 1,000 in base bullion, passing through zero for a bullion about 800 fine.

CHAPTER XIII

THE ASSAY OF BULLION

General.—Bullion is classified as follows:

1. Lead bullion, usually the product of the lead blast furnace; 95 per cent and more lead, containing some copper, antimony, etc., silver, and gold. Unrefined copper containing precious metal is often spoken of as *copper bullion.*

2. Base bullion, containing from 100 to 925 parts of silver per 1,000 gold in varying amounts, and a large percentage of base metals, chiefly copper, zinc, lead, etc. Produced most frequently by cyanide mills.

3. Doré bullion, containing 925 to 990 parts of silver per 1,000, some gold, and base metals, mostly copper, but also lead, antimony, zinc, etc. The term is somewhat loosely applied, bullion with gold up to 300 or more and silver 500 or more being sometimes called *doré.* Some assayers use the word doré for any gold-silver alloy especially the beads obtained in cupellation.

4. Fine silver bullion, free from gold, containing 990 and more parts silver per 1,000, but some base metals, usually copper.

5. Silver bullion, containing little base metal and less than half its weight in gold.

6. Gold bullion, containing little base metal and more than half its weight in gold. Sometimes the gold limit is set at 992.

7. Fine gold bullion, free from silver, containing from 990 to 1,000 parts gold per 1,000.

Silver and gold in all bullions but lead are estimated in parts per thousand, and bullion is said to be so many *parts fine.* Thus, if 1 g. (1,000 mg.) of bullion is taken for assay and it contains 925 mg. gold, it is said to be 925 fine.

In the assay of gold bullion, the *millième* system of assay weights is used, a millième being 0.5 mg., and the assay is reported in parts of 10,000, or the fineness with one decimal added. Thus, the above bullion would be reported as 925.0 fine. In this system, the 500-mg. weight is stamped 1,000; the 250-mg. weight, 500; etc. The scales used must, therefore, be sensitive

to 0.05 mg., or 0.1 millième. This presents no difficulty, as ordinary assay balances are sensitive to 0.01 mg. with a load of 0.5 g.

Lead bullion is recorded in ounces per ton, in the same way as for ores.

The Assay of Lead Bullion

The sample of bullion may be melted under charcoal and granulated in cold water, it may be rolled out into a strip in the rolls and the pieces cut at intervals from this for the sample, or it may be drilled. If lead bullion is free from antimony, zinc, sulphur, arsenic, etc., and contains but little copper, it may be cupelled directly for gold and silver. In this case, four portions of 0.5 a.t. each are wrapped in about 7 g. of sheet lead, placed in the hot cupels, and cupelled with feathers. The cupels are fused with the following charge:

Stained part of cupel	45 g. borax glass
80 g. PbO	2 g. argol
15 g. Na_2CO_3	Thin litharge cover

The buttons from this fusion are cupelled and the weight of the gold and silver added to that obtained from the first cupellation.

If the bullion contains base metals which will influence the results of the cupellation, four portions of either 0.5 or 1.0 a.t. are weighed out and mixed with 30 to 50 g. of test lead; 1.5 g. of borax glass and 0.5 g. of silica are put on top of the lead; and the charge scorified. The resultant buttons, which should weigh about 15 g., are then cupelled. The scorifier slag and cupel are reassayed by the above charge and the correction added.

The Assay of Silver Bullion[1]

The assay of silver bullion is also applicable to base bullion, doré bullion, etc.

Cupellation Method.—This method is used as an approximation for bullions in which silver is to be determined accurately, serving as a preliminary assay for the salt titration, mint, or Gay-Lussac method.

a. Preliminary Assay.—Exactly 500 mg. of bullion are weighed out on an assay balance in order to save calculation, wrapped in

[1] For sampling of silver bullion, see The Assay of Gold Bullion, later in this chapter.

10 g. of sheet lead, and cupelled at 850° C., or with ample feathers of litharge. The silver bead is cleaned, weighed, and parted in 1:9 HNO_3 for at least 20 min.; then, if any gold shows, heated for 5 min. more in concentrated acid, washed, and the gold dried, annealed, and weighed. The amount of gold found, subtracted from the weight of the bead, gives the approximate silver, and the weight of the bead, subtracted from the amount of bullion taken (500 mg.), gives the base metal. This base metal is usually copper, and its presence may be detected by the coloring of the cupel.

b. Making the Check Assay.—As the loss of silver and gold is a question of temperature, amount of precious metal present, amount of lead of cupellation, and amount and kind of base metal present, it is desirable to have the regular cupellation, accompanied by a check assay, made up as nearly as possible to the composition of the bullion to be assayed and cupelled under the same conditions. The check assay is, therefore, made up from data obtained in the preliminary assay. As the silver determined in this preliminary assay is low, due to absorption and volatilization, a correction of 1.2 per cent is added as an approximation, or, rather, the amount of Ag found is considered as 98.8 per cent of that present, and this amount of proof silver weighed out. To this is added, in proof gold, the amount of gold found in the preliminary assay. The difference between the sum of the corrected silver and the gold and 500 is the amount of base metal to be weighed out for the check. As already stated, the base metal is usually copper, and in making up the check c.p. sheet copper is used. The check thus weighs 500 mg. and approximates very closely the composition of the bullion. Duplicates of 500 mg. of bullion are now weighed out, and these and the check each wrapped in the proper amount of sheet lead, as determined from the table below.

TABLE L.—LEAD RATIO IN CUPELLATION

Fineness in silver, milliëmes	Amount of copper present, milliëmes	Amount of lead for cupellation, grams	Ratio of lead to base metal
1,000	0	3	
			140:1
900	100	7	
			120:1
800	200	12	
			72:1
500	500	18	
			60:1
300	700	21	

c. The Assay.—Three cupels are placed in a row across the muffle, so as to be exposed as nearly as possible to the same temperature, and three more cupels are placed near them to act as covers for the cupellation when finished, in order to prevent sprouting. When the cupels have had all volatile matter expelled, the assays are dropped into them, the check in the center one, and the cupellations carried on in the usual way, with feathers. After the blick, the cupels are drawn to the front of the muffle and covered with extra cupels. Sprouted buttons must be rejected. The beads are now cleaned, weighed, and rolled out, parted in flasks, with the acids as described for the preliminary assay, and the gold weighed.

The difference between the silver actually used in the check and that found by assay is the correction to be added to the mean silver result of the two bullion assays made, which should not differ by more than a millième (0.5 point fineness). This correction may be plus or minus, according to the amount of copper in the bullion; for with much copper, some of this may be retained by the silver and give rise to a minus correction. The gold is corrected in the same way as the silver. The subtraction from 500 of the sum of the corrected silver and gold gives the amount of base metal. The individual results obtained express the assay results in fineness.

When metals of the platinum group are present, the method must be modified as outlined, in Chap. XIV, for the assay of platinum, etc.

Wet Methods: Gay-Lussac or Mint Method.—This method is a most accurate one and is based on the complete precipitation of silver as the chloride in a nitric-acid solution by means of sodium chloride. The reaction is as follows:

$$AgNO_3 + NaCl = AgCl + NaNO_3$$
$$1 \text{ part } Ag = 0.542 \, NaCl$$[1]

The standard solution of NaCl usually employed is of such strength that 100 cc. precipitate 1 g. of Ag, so that 5.4207 grams of c.p. NaCl are dissolved per liter of distilled water to give the standard solution. Aside from the standard solution mentioned, there is required another of one-tenth its strength (obtained by taking 1 part of the standard salt solution and

[1] 0.542 seems near enough; 1927 molecular weights give 0.54184. Chaudet, in 1835, gave 0.5474; Stas gave 0.54207.

adding to it 9 parts of distilled water) and an acidulated solution of $AgNO_3$ (obtained by dissolving 1 g. of proof silver in 15 cc. of HNO_3, 1.26 sp. gr., and diluting with distilled water to 1,000 cc.). It follows from the above that 1 cc. of the one-tenth solution will just precipitate the Ag in 1 cc. of the acidulated silver-nitrate solution.

The standard NaCl solution is termed customarily, though incorrectly, the *normal salt solution* in the assay; the weak solution is termed the *decimal salt solution*, and the silver nitrate solution the *decimal silver solution.*

Standardizing Solutions.—The apparatus required is

1. A large bottle or carboy, containing the normal salt solution placed on an elevated shelf so that the solution may be siphoned by means of glass tubing and rubber hose to the main 100-cc. pipette.

2. Liter bottles containing, respectively, the decimal salt and the decimal silver solutions.

3. An accurate 100-cc. pipette (Stas pipette), clamped to a suitable stand and provided at the top with a glass overflow cup containing a moistened sponge to catch the overflow of the normal salt solution.

4. Two small graduated 10-cc. pipettes, one for the decimal salt and one for the decimal-silver solution. Burettes may be used in place of these.

5. A number of strong 8- to 12-oz. bottles, similar to reagent bottles, provided with rubber corks.

The standardizing of solutions is carried out as follows: Two portions of exactly 1,002 mg. proof silver are dissolved in 15 cc. 1.26 sp. gr. HNO_3, the nitrous fumes are removed by boiling, the solution is transferred to the titration bottles, and water added to bring up the amount of solution to 125 cc. The 100-cc. pipette is then filled with normal salt solution to the mark, after washing out with salt solution to prevent dilution. The filling is done by fastening the siphon hose to the bottom of the pipette, opening the clamp on the hose, and letting the pipette fill, with a little overflow. The solution is then shut off by clamping the hose, a finger placed on the top opening of the pipette to prevent the solution from running out, and the hose removed. The pipette is then permitted to drain to the 100-cc. mark, and the solution held there by closing the top of the pipette with the finger The bottle containing the dissolved proof silver is then

placed under the pipette and the normal salt solution permitted completely to drain into it. The bottle is then violently shaken for 3 or 4 min., either by hand or a mechanical agitator, and the AgCl allowed to settle, leaving the supernatant liquid clear. If the normal solution is made up correctly, it will have precipitated just 1,000 mg. of silver, leaving 2 mg. unprecipitated. One cubic centimeter of decimal salt solution is now added to the bottle by means of one of the 10-cc. pipettes or a burette, which, if the solution still contains Ag unprecipitated, gives rise to a white cloud of AgCl. The bottle is again shaken, the precipitate allowed to settle, and another cubic centimeter of decimal salt solution added. If this fails to give a precipitate, then 100.1 cc. of normal salt solution are equivalent to 1,002 mg. of silver (1 cc. of decimal salt solution = 0.1 cc. normal salt solution). If the second addition of decimal salt solution gives a precipitate, the shaking and settling are repeated, and a third and fourth, etc., addition made, until no further cloud appears. The assayer soon learns to judge by the density of the cloud whether only part of the cubic centimeter has been used up. In this way, he should be able to judge to the fourth of a cubic centimeter or the half of a milliéme. If the first addition of decimal salt solution fails to give a precipitate, the normal solution contains an excess of salt, and 2 cc. of decimal silver solution are now added, one of which neutralizes or precipitates the 1 cc. of decimal salt solution first added, the other acting on the excess of salt in the solution. The decimal silver solution is added until no further cloud appears, in the same way as described for the decimal salt solution. In this way, the exact strength of the normal salt solution is determined in duplicate. If it is incorrect to the extent of more than 2 points fineness either way (*i.e.*, either strong or weak), it is corrected by the addition of either water or salt, and restandardized, and, when correct, a new decimal salt solution made up from it. Its strength is finally recorded on the bottle as follows: 100 cc. = 1,001 mg. Ag, or whatever it may actually be.

The Assay.—It is evident from the preceding that the amount of bullion to be taken for assay must contain as nearly as possible 1,000 mg. Ag in order to make the titration with solution as short as possible and avoid undue additions of the decimal solutions. For this reason, the bullion on which the silver determination is to be made is first assayed by the cupellation

method, or at least a preliminary assay, described under this method, is made, and from these data the amount of bullion containing 1,000 mg. of silver calculated. For instance, suppose the cupellation method shows the bullion to be 900 fine in silver; then

$$900:1{,}000::1{,}000:x$$

fineness:amount of bullion::silver:amount of bullion

or 1,111.11 mg. bullion contains 1,000 mg. Ag. This amount of bullion is then weighed out in duplicate and dissolved in acid, placed in titration bottles, as described above under Standardization of Solutions, and titrated.

The calculation for fineness is as follows: Suppose the strength of the normal solution is 100 cc. = 1001 mg. Ag and that 99.8 cc. of normal solution were used in the titration (100 cc. normal salt, and 2 cc. decimal silver); then

$$100:1{,}001::99.8:x$$

the x, or amount of silver in bullion, equaling 998.99 mg.; and the fineness is

$$1{,}111.11:998.99::1{,}000:y$$

the y, or fineness, equaling 899.1.

The only metal interfering with the salt titration is mercury, which will be precipitated by the NaCl as Hg_2Cl_2; the addition of 10 g. cc. sodium acetate and a little free acetic acid to the assay will prevent the precipitation of the mercury. Mercury can be detected in the titration if the AgCl has not turned dark as the result of exposure to sunlight. It will be found sometimes in mill bullions which have been retorted at a too low temperature. The assay and standardization of the solution should be carried out where there is no direct sunlight and where light is not too strong. T. K. Rose[1] showed that the Gay-Lussac method as commonly conducted at mints was accurate to within 0.2 to 0.3 per 1,000; with great care it and also the Volhard method are reliable to 0.1 per 1000, cupellation to about 0.5 per 1000.

The Assay of Gold Bullion for Silver by a Wet Method.—In bullion containing a large proportion of gold, the estimation of silver by the fire method above gives results which are not always so accurate as could be desired. The Gay-Lussac method is generally not applicable on account of the large amount of

[1] *Trans.* I. M. M., vol. XVI, p. 160.

bullion that must be taken for a sample in order to get 1 g. of silver. Direct determination of silver by the following wet method[1] will yield good results: Take 0.5 g. of the bullion, fuse with 1.5 g. of pure cadmium under a cover of potassium cyanide in a porcelain crucible in the flame of a blast lamp. Enough cyanide must be used to cover the cadmium. Five minutes is sufficient to insure fusion. Allow to cool, place in a stream of running water which will rapidly dissolve the cyanide, and leave the alloy. Transfer this to a flask with 20 cc. of water, add 40 cc. of HNO_3 in installments of 10 cc. each while boiling for 1 hour. Dilute to 150 cc. and add 10 cc. of ferric-alum indicator and titrate with the standard solution of NH_4CNS. This solution is made as follows: 1.6 g. of pure NH_4CNS are dissolved in 1,000 cc. of distilled water. This is standardized against pure silver foil dissolved in HNO_3 and diluted to 150 cc., one cubic centimeter of the solution equals approximately 4.483 parts of Ag per 1,000 under the conditions described above. The indicator is a saturated solution of ferric alum. The appearance of the red color marks the end point. Copper in amounts of 100 parts per 1,000 in the bullion does not interfere with the delicacy of the end point. In case the bullion is very high in gold, the cadmium must be increased. The parted gold is recovered from the residues in the flasks.

The direct determination of silver in gold bullion presents some difficulties, as the bullion is not soluble in either nitric acid or aqua regia, and inquarting with silver is out of the question. Solubility of the silver in nitric acid may be secured by alloying with a base metal which will not interfere with titration of the silver. Several procedures have been suggested employing either zinc or cadmium, the latter being preferable. One of the most expeditious is the following, which is practically the method adopted in 1911 by the U. S. Mint in San Francisco.[2]

Weigh out samples of 0.500 g. bullion and wrap each in about 1 g. lead foil. Cut stick cadmium into pieces of about 5 g. each. Take small scorifiers and in each put enough sodium cyanide or "98 per cent potassium cyanide" to half fill it when melted. Place these in the front row of a muffle and heat to moderate redness but not enough to boil the fused cyanide. Drop in the

[1] Taylor, E. H., *Australian Mining Standard*, vol. XL, p. 235, 1908; consult, also, Clennell, J. E., *Eng. Mining Jour.*, vol. LXXXIII, p. 1099.

[2] *Ann. Rept.*, Director of the Mint, U. S. Treasury, p. 33, 1912.

lead foil containing bullion and immediately add the cadmium. After a minute or two, take up each scorifier with tongs and give it a slight rotary motion to insure mixing, then pour into an iron mold. As soon as set, tap the cyanide to detach it; it may be used a second and third time. Treat the button with boiling water to remove all cyanide, wash well, place in a 250-cc. flask, and dissolve in about 60 cc. nitric acid (sp. gr. 1.28 or about 1:1) on a hot plate. Boil off red fumes, add about 100 cc. distilled water and 2 or 3 cc. saturated solution of iron alum or ferric sulphate. Titrate with a standard solution of potassium or ammonium thiocyanate. If 1 cc. is equivalent to 0.005 g. silver, the number of cubic centimeters used multiplied by 10 gives the silver fineness of the bullion.

It is equally convenient to use samples of 1.000 g. and to make the titrating solution of 0.76 per cent NH_4CNS (about 8 g. of the crystals per liter) so that 1 cc. = 0.010 g. silver. In some offices where the Gay-Lussac system is in daily use, enough pure silver is weighed out to make the total silver about 1 g. and this is dissolved with the other in the flask. After determining the total exactly, the amount added is subtracted.

Instead of using a scorifier, the cadmium and bullion may be alloyed in a porcelain crucible over a bunsen burner, under a smaller amount of cyanide; the latter is then dissolved off as soon as cold.

The Assay of Gold Bullion

1. *Sampling.*—Bullion in the form of bars and retort sponge, as received at the United States assay offices and mints, is remelted into bars to make the deposit uniform. These bars are sampled by taking from diagonally opposite corners chips, each of which is rolled into a fillet and assayed by different assayers, who are required to check with each other within narrow limits; if they do not, the bar is remelted, stirred thoroughly, and recast, then sampled again and assayed. If base bullion, or one which liquates seriously on cooling, is to be assayed, dip samples are taken from the molten bullion by means of a small graphite ladle, and the sample granulated in warm water. Silver bullion is sampled in the same manner.

2. *Preliminary Assay.*—This is made in the way described for silver bullion, except that in the assay of gold bullion no determination of silver is made by cupellation; but if this is to

be determined, the mint wet method is used. Experienced assayers can judge the approximate fineness of gold bullion by the color and add the proper amount of silver necessary to insure parting. In the San Francisco mint, 2 parts Ag to 1 part Au are used.[1] The British royal mint formerly used 2.75 parts

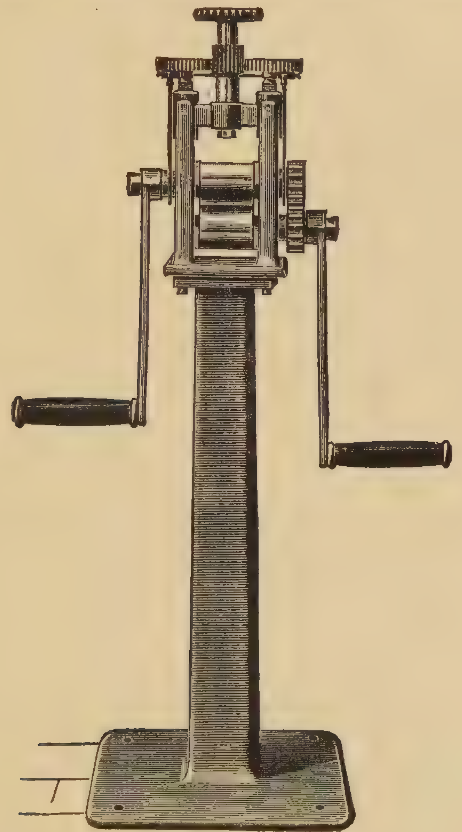

FIG. 58.—Jewelers' rolls. The Calkins Company of Los Angeles furnishes jewelers and bullion rolls that may be tilted so that the button can be fed into the rolls either vertically or horizontally.

Ag to 1 part Au,[2] but now uses 2:1. More than 3 parts Ag to 1 part Au should not be used; otherwise, the "cornet" (spiral) of gold is apt to break up. With less than 2 parts Ag, too much Ag is retained, although with continued boiling 1.75 parts Ag will

[1] PACK, JOHN W., "Assaying of Gold and Silver in U. S. Mint," *Mining Sci. Press*, vol. LXXXVII, p. 317.

[2] ROSE, T. K., *Eng. Mining Journal*, vol. LXXX, p. 492.

part Au from Ag.[1] For the preliminary assay, 500 mg. (1,000 millièmes) are weighed out, silver added according to judgment to bring the ratio of silver to gold to 2 or 2.5 (allowing for silver in the alloy), and the bullion and silver wrapped in 10 g. sheet lead and cupelled at 850° C.

The resultant bead is cleaned, weighed, flattened, and rolled out in jeweler's rolls to a fillet of the approximate thickness of a visiting card. If some copper is present in the bullion, enough is retained by the gold bead to toughen it, and it can be easily rolled without cracking, if, between reductions by the rolls, the fillet is annealed at a dull-red heat. The presence of copper in the button aids in the total removal of lead during the cupellation.[2]

The fillet is then again annealed and rolled into a cornet and parted in a parting flask. This is filled with 30 cc. of HNO_3, sp. gr. 1.20, free from Cl, H_2SO_4, H_2SO_3, or any sulphide, and heated to boiling (or at least 90° C.) for 20 min. The acid is then decanted off, and the cornet washed carefully twice with hot distilled water by decantation. Then 30 cc. of boiling nitric acid, sp. gr. 1.30, are added to the flask, and the cornet boiled again for 20 min., after which the acid is decanted, and the washing with hot water repeated several times. During the boiling, a charred pea added to the flask prevents bumping. Still better is a roughly broken fragment of Acheson graphite or a bit of electric-light carbon, previously extracted with nitric acid. These can be used repeatedly. The flask is now filled to the very top with cold distilled water, a suitably sized porcelain parting cup placed over the mouth, fitting reasonably tight, and the flask inverted. The cornet will settle into the parting cup, and the flask is then gently tipped to permit the water to escape, the water is decanted from the parting cup, and the cornet gently dried. When dry, the cornet is transferred to a clay annealing cup, the cover is put on, and the cup is placed in the muffle, and the cornet annealed at a full-red heat. It is then weighed. The weight of the gold plus that of the added silver, subtracted from the weight of the cupelled bead, gives the approximate amount of silver in the assay. This added to the weight of the gold and subtracted from 500 mg. (the weight of bullion taken) gives the approximate amount of base metal. If the amount of silver

[1] Rose, "Metallurgy of Gold," p. 493.

[2] Rose, "Refining Gold Bullion," *Trans.* I. M. M., vol. XIV, p. 377, 1905.

added to part the gold has raised the ratio of Ag:Au over 3:1, the gold will probably have broken up, or at least parts will have broken from the edges of the cornet; care, in this case, must be taken to collect all of it in the washing. If the results show that the ratio of Ag:Au has been less than 2:1, the cornet must be recupelled with 2.5 parts Ag and parted as described.

The Assay.—The final assay is made up from data obtained in the preliminary assay. Duplicates on 1,000 millièmes are run, with a check assay made up in composition as near to that of the bullion as possible, as described for the cupellation assay of silver. In making up the check, proof gold and proof silver are used, and pure copper foil or wire. The United States mints use various proof alloys in the making up of check assays. For the assay of fine gold bars (990 fineness and above), a proof alloy of 1,000 gold, 2,000 silver, and 30 parts copper is used. For coin metal (900 parts fine), a proof alloy of gold 900 parts, silver 1,800 parts, copper 100 parts is used. For the determination of base metal (the difference between the gold and silver and the 500 mg. taken for assay), a proof alloy of gold 900 parts, silver 90 parts, copper 10 parts is used.[1] In this last, the gold need not be proof gold but may be remelted cornets. It is to be noted that these proof alloys are made up on the assumption that 2 parts Ag:1 part gold are used in parting. The British Mint uses a proof alloy, or trial plate, 916.6 fine in gold for the assay of coin bullion.

For the assay of crude gold bullion, *i.e.*, mill bullion, the proof alloy for fine gold bars is generally used.

The amount of lead used in the cupellation is as follows:[2]

Table LI.—Lead Ratio in Cupellation

Amount of gold per 1,000 parts, milligrams	Amount of lead, grams	Ratio of lead to copper (base metal present)
916.6	8	96 to 1
866	9.15	68 to 1
770	14.75	64 to 1
666	16.00	48 to 1
546	17.50	38 to 1
333	18.00	27 to 1

[1] Pack, John, *ibid.*
[2] Rose, "Metallurgy of Gold," p. 494, 1902.

To the duplicates of the 1,000 millièmes of bullion the proper amount of Ag is added, to bring the ratio of Ag:Au to 2:1,

and then they are wrapped in the proper amount of c.p. sheet lead. The check is made up as indicated by the preliminary assay, and the three assays cupelled as described for the assay of silver bullion. The three beads are then treated and parted, as described for the preliminary assay. The two bullion assays should not differ by more than 0.25 part of a millième. The correction as indicated by the check should then be applied, whether this be plus or minus. The difference between the fine gold in the check and that obtained by the assay of the check is the surcharge, which is more definitely defined in Chap. XII, on Errors in the Assay for Gold and Silver. This surcharge will usually amount to about zero for a bullion of about 700 to 800 fine; above that there will be a "plus surcharge," and below that a "minus surcharge." The plus surcharge will be subtracted and the minus surcharge added.

In place of taking the precise amounts of lead indicated in Tables L and LI, many assayers obtain equally satisfactory results by keeping sheet lead cut into five or six gram pieces and using one, two, or three of these for 500 mg. of bullion, to approximate the same ratios of lead and precious metal.

For the determination of gold and silver in dorè bars which contain too little gold to give coherent residues on parting, assay offices commonly adopt a practice which will bring the work into line with their usual routine. Either 500 or 1,000 mg. may be weighed out. For gold, some add a known weight of fine gold which will bring the total gold up to a parting ratio of 2.5 or 3 and inquart by cupelling. For silver, some add more fine silver to the flask when dissolving to bring the total to about 1.000 g. and determine this total by the Gay-Lussac method. Others rely on the fire assay for silver and gold and weigh the parted gold directly, which with proper proofs gives results that are usually satisfactory, the silver being obtained by difference; others prefer to titrate the silver with thiocyanate. As a rule, all of these methods give fairly concordant results, but occasionally a sample is found which shows discrepancies.[1]

Proof Gold and Silver.—Gold and silver of the highest degree of purity may be purchased from the U. S. Mint at Philadelphia, where they are specially prepared for use as proofs. The gold costs about $40 and the silver about $1 per ounce above the market price of the metal.

[1] See DEWEY, "Determination of Silver and Base Metal," *Jour. Ind. Eng. Chem.*, vol. VI, pp. 650, 728, 1914.

CHAPTER XIV

THE ASSAY OF ORES AND ALLOYS CONTAINING PLATINUM, IRIDIUM, GOLD, SILVER, ETC.

Materials containing some of the above elements are presented to the assayer for determination in the shape of sands containing chiefly platinum, alloys, and jewelers' sweeps, and, more rarely ores containing platinum in the form of the mineral sperrylite, etc.

The assay for platinum and associated metals is a difficult one, due to the fact that in the parting of the precious metal beads, by acids, complex reactions take place, by which platinum, palladium, silver, etc., both go into solution and are retained in the residue, unless certain well-established ratios of metals present are observed and the parting operation repeated several times. The alloys of platinum and silver have been most thoroughly investigated in this connection.[1] When the alloy is more complex, *i.e.*, contains also gold, palladium, iridium, rhodium, etc., the difficulties of the assay are increased; the data at present available are meager.

Platinum nuggets from the Urals contain:[2] Pt, 60 to 86.5 per cent; Fe, up to 19.5 per cent; Ir, up to 5 per cent; Rh, up to 4 per cent; Pd, up to 2 per cent; also Os, Ru, Cu, Au, and iridosmium.

When material containing Au, Ag, Pt, Pd, Ir, Rh, Ru, Os, and IrOs is fused by the crucible assay or melted with lead, the Au, Ag, Pt, Pd, Ir, Rh, IrOs are collected by the lead and the Ru, and Os only partially so. If the resultant lead button is cupelled, the final bead will contain the Au, Ag,[3] Pt, Pd, Ir, Rh, IrOs, and a comparatively small portion of the Os and Ru, the most of these two metals being lost by oxidation. The presence of any considerable amounts of Os and Ru in the lead button, owing to

[1] THOMPSON and MILLER, in *Jour. Am. Chem. Soc.*, vol. XXVIII, p. 1115. See this paper for other references.

[2] KEMP, in *Eng. and Min. Jour.*, vol. LXXIII, p. 513 (Notes on Platinum and Associated Metals). U. S. Geol. Surv. *Bull.* 193, pp. 18–19, 1912.

[3] Exclusive of losses by absorption and volatilization.

the fact that they will not alloy readily, causes them to appear as a black scum or as spots on the bead, near the end of the cupellation. The presence of the platinum group of metals, raising the melting point of the gold-silver alloy, renders necessary a high temperature of cupellation in order to remove lead. Even then, when the ratio of Ag to Pt, etc., is less than 5 to 1, lead will be retained in varying proportions at the cupellation temperature of gold bullion. To get rid of the lead, the proportion should be 10 to 1.[1] The following points on the first cupellation of the lead buttons, resulting from the assay of material containing Pt, etc., will give the assayer an idea of what is present. When Pt alone, or with very little silver is present, the bead from the cupellation (at a comparatively high temperature) is rough, dull gray, flat, and contains lead.

If more silver is present, but less than 2 parts of Ag to 1 of Pt, the beads are rough, flat, and have a crystalline surface.

If more than 2 parts of Ag are present and not more than 15, the bead approaches more nearly the appearance of a normal silver bead, but has a more steely appearance and is flatter in proportion to the Pt, etc., contained.

Beads containing more platinum than 1 in 16 will not blick or flash.[2]

The effect on the appearance of the bead of Pd, Rh, Ir is similar to that of Pt, but not identical.

Owing to the difficulty in alloying iridium, this, when present, is apt to be found at the bottom of the bead, in the shape of fine black crystalline particles.[3]

The Action of Acid on the Alloy Beads.—A great deal of literature exists on this point; but most of it is very conflicting; some facts, however, have been definitely established.

Nitric Acid.—In an alloy of Pt and Ag treated by HNO_3, platinum goes into solution in various proportions, depending on the ratio of Ag to Pt, and probably to some extent on the strength of acid. It has been stated that when the ratio of Ag to Pt is 12 or 15 to 1, this solution of Pt is complete in one treatment, but this has been disproved by later investigation.[4] In order to accomplish the solution of Pt, the acid treatment

[1] Sharwood, "Cupellation of Platinum Alloys, containing Ag and Au," in *Jour. Soc. Chem. Ind.*, vol. XXIII, p. 412.

[2] Schiffner, in *Mineral Ind.*, vol. VIII, p. 397.

[3] Rose, "Metallurgy of Gold," p. 514.

[4] Thompson and Miller, in *Jour. Am. Chem. Soc.*, vol. XXVIII, p. 115.

must be repeated at least once or twice, with a possible recupellation of the residue with silver before the second treatment. It is even then doubtful if all of the Pt can be dissolved. The Pt goes into solution in the nitric acid in colloidal form, giving a brown to blackish color to the solution. When gold is present in the silver-platinum alloy, the solubility of the Pt seems to be decreased,[1] unless the ratio of Pt to Au to Ag is 1:2:15,[2] when most, but not all, of the Pt and all the Ag go into solution. Palladium goes into solution with nitric acid when at least 3 parts of Ag to 1 of Pd are present,[3] yielding an orange-colored solution; but double parting is necessary to insure complete solution. (This point is not sufficiently established.[4]) The orange-colored solution indicates colloidal palladium.

Iridium and Rhodium.—Iridium present in the beads is unacted upon by HNO_3 and remains with the gold.[5] Rhodium is slightly dissolved, but most of it remains with the gold. Iridosmium is not dissolved. Osmium is dissolved. Ruthenium is not dissolved.

Sulphuric Acid.—Platinum, alloyed with silver and gold, can be separated from the silver and remains with the gold, if concentrated sulphuric acid is used in parting. In order to insure thorough parting, at least 10 parts of silver to 1 part Pt and gold should be present, and double parting resorted to, otherwise silver will remain with the residue.[6] The parting in H_2SO_4 leaves the Pt and gold in a very fine state of division (but not as a colloid), some of which is very apt to be lost in decanting, so that it is best to separate by filtering through an ashless filter. It is also to be noted that lead may be present in consequence of a too low cupellation temperature, in which case the residue should be treated with ammonium acetate, to remove lead sulphate.

Palladium.—In parting with H_2SO_4 this goes into solution with the silver, giving an orange-colored solution. Whether this solution is complete, has not as yet been demonstrated.[7]

Ir, IrOs, Rh, and Os and Ru in the bead are not dissolved.

[1] SHARWOOD, *ibid.*

[2] LODGE, "Notes on Assaying," p. 215.

[3] ROSE, "Metallurgy of Gold," p. 514.

[4] LODGE, "Notes on Assaying," pp. 218, 219.

[5] ROSE, *ibid.*

[6] THOMPSON and MILLER, *ibid.*

[7] LODGE holds the contrary, p. 219.

Nitro-hydrochloric Acid.—From the residue of the sulphuric acid parting, the Pt, Au, and any Pd left is dissolved by dilute aqua regia, 1 to 5, leaving Ir, IrOs, and Rh, and some Ru and Os, if present. This last residue, treated with strong aqua regia, removes Ir, leaving iridosmium and rhodium as a final residue.

There has been much activity within recent years in the search for platinum owing to the high price of the metals of the platinum group. This has focused attention on methods of assaying and the United States Bureau of Mines investigated the subject.[1] A thorough bibliography was[2] published by the United States Geological Survey.

Methods of Assay. 1. *Ores.*—Rich ores, carrying Pt, etc., in grains, present difficulty in sampling, inherent to any ore containing "metallics." It is best to take from 30 to 50 g. of the sample and fuse it with six times its weight of lead in a crucible, fluxing the gangue. The lead is poured, and after cooling the slag is detached carefully, the lead platinum alloy being brittle, weighed and remelted under charcoal in order to insure a uniform alloy, and then granulated as fine as possible by pouring into a large volume of cold water from a considerable height. The resultant sample is then dried and is ready for assay. An amount containing approximately 200 mg. Pt is weighed out and scorified with 50 g. Pb into a 20-g. button.

If, in the low-grade ores, the Pt, etc., is present as grains, a weighed quantity is concentrated by panning and the concentrates scorified with twenty to twenty-five times their weight of test lead, and the button treated according to method No. 1 or 2, as below. If the ore contains the rare metal in other form, crucible fusions are made on 1 assay ton, as with gold and silver ores, and if very low grade, the buttons from four to five fusions are scorified into one button, final duplicates being made as usual. The lead buttons are treated as below.

[1] Davis, C. W., "The Detection and Estimation of Platinum in Ores," U. S. Bur. Mines, *Tech. Paper* 270, 1921.

Lind, S. C., C. W. Davis, M. W. von Bernewitz, "Platinum Assays and Platinum Promotions," U. S. Bur. Mines, Rep. of Investigations, Ser. 2496, July, 1923.

Davis, C. W., "The Estimation of Platinum in Ores Containing Copper," U. S. Bur. Mines, Rep. of Investigations, 2228, 1921.

[2] Howe, J. L. and H. C. Holtz, "Bibliography of the Metals of the Platinum Group," U. S. Geol. Surv., *Bull.* 694, 1919.

2. *Alloys.*—An amount of drillings or filings (representing a true sample of the alloy), containing, if possible, not to exceed 200 mg. of Pt, etc., is weighed out and scorified with 80 g. of test lead, to a button of about 18 to 20 g. The lead buttons are treated as outlined below.

First Method.—The lead button obtained by any of the foregoing methods is cupelled at a temperature of at least 900° C., or, better, 950° C., and the resultant bead examined. If, from the foregoing description of the appearances of a bead, it is thought that the ratio Ag to Pt, Au, etc., is less than 10:1, the button is removed, the necessary silver added to bring it up to the above ratio, recupelled with 5 to 8 g. of lead at a temperature of 900° C., and weighed. The bead is then flattened and rolled out into a cornet, if large and not too brittle, and parted with 15 cc. H_2SO_4 concentrated, boiling for 15 to 20 min. The acid is then decanted into a beaker and saved, the residue re-treated with 5 cc. more of acid for 10 min., and the residue and acid washed into the beaker containing the first acid. The acid is then diluted and the residue separated by filtration through a small ashless filter, and thoroughly washed with hot water to insure removal of Ag_2SO_4. The filter paper is dried and carefully transferred to a porcelain parting cup or an annealing cup, and the carbon burnt off in the muffle. The annealed residue is brushed out on the scale pan of the bead balance and weighed. It consists of gold, platinum, iridium, iridosmium, rhodium, and possibly osmium and Ru (if any escaped oxidation during the cupellation), and perhaps some palladium. Its color will be gray or black, if the rare metals are present to any extent. If not, the characteristic gold color will show. The palladium is largely in the filtrate. (It is questionable how complete this solution is.[1]) If it has been unnecessary to add Ag to the cupellation to get the 10:1 ratio, the difference in weight between the original bead and the weight of the residue represents the Ag. If silver had to be added and the bead recupelled, the weight of the added silver plus that of the residue, subtracted from the weight of the recupelled bead, gives the silver. Allowance, however, must be made for considerable loss of silver as a result of high cupellation temperature. If accurate silver results are required, a duplicate assay on the

[1] Ricketts and Miller, in "Notes on Assaying," state that the Pd dissolves with the Ag.

material must be run, and the silver requisite to bring the ratio up to 10:1 is added at once to the lead button, one cupellation only being made. At the same time this is run, a check assay is run beside it, made up of the same weight of lead, and the proper weight of silver, *i.e.*, the amount added to the first cupellation plus the amount approximately known to be in the assay. The loss in this will give the correction to be added to the assay for Ag. It may be desirable to determine Ag in the wet way (see "The Assay of Silver Bullion").

The residue is now wrapped in 8 to 10 g. of lead foil with at least twenty times its weight in silver and cupelled again at a high temperature. The bead, if large, is rolled out and heated to boiling in a mattrass or flask for 20 min. with HNO_3, sp. gr. 1.20, after which the acid is decanted into a beaker, and the treatment repeated with HNO_3 of sp. gr. 1.26. The residue, if finely divided, should now be filtered through an ashless filter and washed as already described. If not, the filtrate can be decanted and the residue washed. The residue consists of Au, Ir and iridosmium, and some Rh and Ru. If there is a suspicion that any platinum, etc., remains, the residue must be retreated with acid until of constant weight. The platinum is in the filtrate, which will be colored brown or black.

The difference between the weights of the first and second residues is platinum, the result possibly being somewhat high if palladium is present in the material assayed. The second residue is now warmed in a mattrass with dilute aqua regia[1] (1:5) for 15 min. This dissolves the gold, some of the Ru, and very little Rh, leaving the Ir, iridosmium, and Rh, with some Ru. The residue is either filtered or decanted, as necessary, dried, annealed, and weighed. The difference in weight between the second and third residues represents gold, somewhat high, if the Ru has partly escaped oxidation and volatilization during cupellation. The gold can be recovered by precipitation with oxalic acid, as described in the second method.

If the third residue is treated with strong aqua regia, and boiled, it dissolves out the iridium, leaving as a residue the iridosmium and most of the Rh. This is dried, annealed, and weighed, the difference in weight between the third and fourth residues representing iridium, and the weight of the fourth residue

[1] Concentrated aqua regia is one part HNO_3, sp. gr. 1.42, and three parts HCl, sp. gr. 1.20.

representing iridosmium and Rh. The method determines Ag, Pt, Au, Ir, and iridosmium plus Rh. The probable errors in the determination have been pointed out. Palladium can be satisfactorily determined only by wet analysis.

Second Method.[1]—Take the lead button from the ore or alloy assay, and scorify at a high heat, with additional test lead, if necessary, to a weight of 8 to 10 g. It should contain less than 5 per cent Pt. etc., in order to be malleable. Roll out the button into a long, thin fillet and place in a large beaker with 200 cc. of HNO_3, sp. gr. 1.08,[2] and heat until all action ceases. Filter through a small ashless filter and wash the residue with hot water. Dry the residue and paper, transfer to a large-sized parting cup and ignite in the muffle, to burn off the carbon, and oxidize any Pb not dissolved. Then heat to boiling in the cup with HNO_3, sp. gr., 1.08, decant, wash thoroughly with hot water, dry, anneal, and weigh the residue. This consists of Au, Pt, Ir, iridosmium, and most of the Rh, as well as the Ru and Os which escaped oxidation and volatilization during the scorification. The filtrate contains the Ag and Pd and a little of the Rh.

Replace the residue in the capsule and warm (not boil) with dilute aqua regia (1:5) for 10 min. This dissolves the Au and Pt. Decant the solution into a small beaker, wash the residue, dry, anneal, and weigh. The second residue consists of Ir, IrOs, Rh, and a little Os and Ru. This residue is boiled with strong aqua regia, which dissolves the Ir and some Os and Ru, and leaves in the third residue the IrOs and Rh, with a little Os and Ru. This is washed, decanted, and weighed as before. The filtrate from the treatment of the first residue, which contains the gold, is evaporated just to dryness, but not baked, so as to prevent reduction of the gold chloride, taken up with distilled water and a drop of HCl, and the gold in it precipitated by warming with crystals of oxalic acid for ½ hour, filtering, and drying the yellow coherent precipitate of gold. This is transferred, filter-paper and all, to a piece of sheet lead, silver added to the weight of three times the gold present, approximately, and cupelled, the bead being parted in HNO_3 as usual and the gold annealed and weighed. The weight of the gold, subtracted from the difference in weight between the first and second residues is the platinum. This last may also be estimated by

[1] Miller, E. H., in *School of Mines Quart.*, vol. XVII, p. 26.

[2] 81 parts distilled H_2O to 19 parts HNO_3 concentrated (sp. gr. 1.42).

destroying the oxalic acid in the filtrate from the separation of gold, and precipitating as $(NH_4)_2PtCl_6$.[1]

It is to be noted that, by the assay as outlined, neither osmium nor ruthenium can be determined, owing to their volatility during part of the operation; that palladium cannot be readily determined, owing to its varying solubility; and that when rhodium or the above metals are present in any appreciable quantity, some of the results obtained are liable to error. Rhodium, osmium, and ruthenium are among the rarer of the group, and are frequently absent. The methods outlined will serve to determine reasonably well platinum, gold, silver, iridium, and iridosmium plus rhodium. When the other elements of the group are present, wet methods, not within the scope of this book, must be resorted to.

In the ordinary assay, as carried out for gold and silver, platinum and palladium may escape the assayer if present in only small quantities, for obvious reasons. Parting in sulphuric acid is, therefore, necessary to determine whether they are present.[2]

The following method[3] is furnished by Ledoux and Company, New York:

Determination of Platinum, Iridium, Osmiridium, and Gold in Grain Platinum. *Sampling.*—If the material occurs in fine grains of nearly uniform size, relatively free from black sand and without particles of free gold, it may be sampled down directly on a split sampler to about 20 g. which should be accurately weighed and dissolved as described below. On the other hand, if the material consists of both coarse and fine grains, contains much black sand, and shows large particles of free gold, it should be separated into sizes by screening and a 20-g. sample made up by weighing proportional parts from the several sizes. The screens selected will depend, of course, upon the grain of the material; ordinarily, separations into material coarser than 40 mesh, between 40 mesh and 60 mesh, and finer than 60 mesh will be sufficient. A carefully drawn sample of about 500 g. taken by dividing the whole lot on a split sampler may be taken for separating into sizes.

Solution.—If the material has been sampled down directly, without separating into sizes to about 20 g., ascertain the exact

[1] CROOKES, "Select Methods."

[2] An orange-colored solution indicates palladium

[3] Private communication, May, 1913.

weight, but do not adjust it to exactly 20 g. by adding or subtracting portions with a spatula. If the material has been separated into sizes, take exactly 20 g. by carefully sampling each of the several sizes to about the required weight and then adjust by adding or subtracting the required amount of each size separately to make exactly 20 g.

Treat the weighed portion in a large covered casserole on a steam bath with 50 to 60 cc. of aqua regia (four parts HCl to one part HNO_3) until no further action is observed, decant the liquid into a large beaker and retreat the residue with more aqua regia. When nothing more dissolves, decant the liquid into the beaker and again treat the residue with aqua regia. Continue alternate acid treatments and decantations until nothing more can be dissolved. Dilute the liquid in the beaker with water and filter it into a liter flask. Transfer the residue from the casserole into the same funnel and wash it well with warm water. Set the solution in the liter flask aside (Solution *A*).

Iridium and Osmiridium.—Scorify the insoluble residue remaining on the filter paper at a very high temperature with 80 g. of test lead to obtain a 25-g. button. This removes siliceous matters, iron sand, chromite, and other base materials. Platinum and some iridium alloy with the lead, but osmiridium, together with part of the iridium, remains as unalloyed metal mixed with the lead. The lead button is apt to be brittle (if the platinum metals, insoluble in aqua regia are in large amount); it cannot be flattened by hammering.

Treat the lead button with hot dilute HNO_3 (1 to 5). Lead will dissolve together with a very small amount of platinum. The amount of the latter in most cases is practically negligible. It should, be reclaimed, however, or at least it should be ascertained that the amount is small enough to be neglected.

Filter the nitric acid solution and wash the residue well with hot dilute nitric acid followed by hot water. Set the filtrate aside for recovery of the small amount of platinum in it (Solution *B*).

Burn the filter paper containing the iridium and osmiridium residue and treat the metal again with 60 cc. of aqua regia, the same as at first. Some platinum and a little iridium will be dissolved. Decant the solution into a beaker and again treat the residue with aqua regia. After all soluble platinum metals are dissolved, decant the acid solution into the beaker, dilute the liquid and filter it into solution *A*. Collect the insoluble

residue on the same filter and wash it well with hot dilute, HCl, followed by hot water. Dry and ignite the metallic residue, consisting of osmiridium and the greater part of the iridium, in a weighed porcelain crucible. After ignition, part of the residue will appear black; this may contain iridium oxide (Ir_2O_3). To decompose this, place the weighed porcelain crucible within a larger porcelain crucible fitted with a good cover. Place the larger porcelain crucible in a clay crucible and pack the spaces between porcelain and clay with clean charcoal broken to rice-grain size. Cover the clay crucible and heat it in a muffle to a temperature of 1000° or more for 10 or 15 min. After the clay crucible has cooled, remove and weigh the inner porcelain crucible. After ignition as above, the metallic residue is of a uniform gray appearance, all black particles having disappeared. The loss in weight suffered by heating to a high temperature in a reducing atmosphere is small, usually amounting to only a few milligrams. On the basis of a 20-g. sample, this is practically negligible when calculated to parts per thousand or per cent, but the fact that *finely* divided iridium produced by igniting the residue from the lead button in air is in part oxidized, is worth noting. The oxide is said to be decomposed simply by heating to 1000° or thereabouts but the writer has not verified this statement.

The weighed residue consists of iridium and osmiridium, but it does not contain all of the iridium.

To recover the small amount of platinum and platinum metals which may have passed into solution with lead on treating the lead button resulting from the scorification of the first insoluble residue with nitric acid (Solution *B*) add to this solution an excess of sulphuric acid to precipitate most of the lead, filter and wash the $PbSO_4$ and reserve it. Evaporate the clear liquid until nitric acid is expelled and sulphuric acid fumes are given off. Cool, dilute with water, and filter off the small amount of lead sulphate thus obtained, adding it to the main precipitate of lead sulphate. This precipitate contains a small amount of platinum and some is also present in the acid liquid. Fuse the lead sulphate with soda, silica, and a reducing agent, so as to obtain a small lead button. In the meantime, heat the filtrate from the lead sulphate to boiling and pass H_2S into it, thereby precipitating the platinum metals as sulphides, filter and wash the sulphides and reserve them.

Flatten the lead button from the lead sulphate and treat it with dilute nitric acid (1 to 5). The amount of platinum which dissolves at this point is quite negligible; in fact, it can hardly be detected. A small insoluble residue of platinum will remain. Filter and wash it with dilute nitric acid followed by hot water. Ignite the filter paper together with that containing the platinum sulphide in a small porcelain crucible. Dissolve the platinum in aqua regia and add it to the main aqua regia solution of the sample (Solution A); this now contains all platinum and platinum metals except the insoluble iridium and osmiridium, and all gold contained in the original sample.

Make the volume up to exactly 1,000 cc., mix well and take out 25 cc., with a carefully calibrated pipette, equivalent to one-fortieth of the original sample. A "washout" pipette which *holds* exactly one-fortieth of the volume held by the flask is better for this work than a pipette which delivers the required amount. The former, provided the comparison with the flask has been accurately made, is less liable to measurement errors than the latter. In this case, very careful measurement is required, and one should not only see that the aliquoting apparatus is accurate, but also that the fraction is taken from the flask at the same temperature at which the solution was diluted to standard volume.

Evaporate the 25 cc. contained in a 150-cc. beaker to dryness on a steam bath, add 5 cc. of HCl, and again evaporate to dryness to remove HNO_3. The beaker should be covered for a few moments when the HCl is added to the dry residue to prevent loss from spattering through the rapid evolution of HCl gas.

Gold.—Add 4 or 5 drops of strong HCl and a little water to the residue; it should dissolve to a perfectly clear solution. Dilute it to 50 cc. or thereabouts, add about 1 g. of pure oxalic acid and boil it gently for half an hour. Metallic gold in a fine state of division is thus precipitated; let it settle for several hours; filter it on a double filter and wash it first with a little warm water and then with hot dilute HCl, followed by warm water. A little platinum is carried with the gold, probably retained mechanically by the filter paper and precipitate, rather than actually precipitated as metal. A second separation is necessary. Burn the filter carefully and dissolve the residue in aqua regia, evaporate the solution to dryness, add HCl, and again evaporate to destroy HNO_3, dissolve the residue in water plus a few drops

of HCl, add an excess of oxalic acid, boil for half an hour, and after several hours standing filter through a small double filter into the main platinum solution. Wash the gold as before, transfer the filter to a small scorifier, add pure silver foil or wire amounting to seven or eight times the weight of gold, and a little test lead, scorify so as to obtain a small lead button, cupel, part, and weigh the gold. The dry filter containing the gold may be wrapped in pure sheet lead together with the silver and cupelled directly if preferred, but there is more danger of loss than when the paper is burned in a scorifier. Cupellation with silver and subsequent parting is superior to weighing the gold precipitated by oxalic acid directly because certain impurities such for instance as copper, if copper is present in the original solution, may be included with the precipitated gold, or a trace of silver, soluble in the relatively strong aqua regia solution, but rendered insoluble by evaporation and subsequent dilution may be present. Moreover, the gold obtained by igniting the oxalic-acid precipitate must be weighed in a tared crucible on an analytical balance. The errors made in this way are much greater than the errors incidental to cupellation, parting, and weighing the gold on an assay balance. If a large amount of silver is added, the gold loss due to cupellation is very small.

Platinum.—Add 15 cc. of strong HCl to the united filtrates from the gold separation, heat to boiling, and pass a rapid current of H_2S into the hot liquid. There will be no difficulty in precipitating all platinum metals as sulphides provided the solution is kept hot and plenty of H_2S is used. The precipitate, of course, includes certain base metals, for instance some copper, if copper were present in the original sample, or a little lead derived from the aqua regia treatment of the nitric acid residue from the lead button, since nitric acid alone does not remove the lead completely.

Filter the sulphide precipitate and wash it with hot water. Dry and ignite it very slowly and carefully in a porcelain crucible, finally heating to a good red heat. There is no danger of losing platinum metals when burning the sulphides, provided the ignition is conducted slowly.

Dissolve the metallic residue in dilute aqua regia (1 part HNO_3, 3 parts HCl, 16 parts H_2O) at a low temperature on a steam bath. This requires a long time, usually over night, although complete solution may be accomplished by several hours digestion in the

daytime. The temperature during solution should be kept below 70° C. Platinum dissolves, leaving an insoluble residue of iridium as a fine black powder. Filter through a double filter, wash repeatedly with hot dilute HCl, and finally with water. Ignite the residue carefully in a small tared porcelain crucible. The metal will be black and undoubtedly is, at least in part, iridium oxide. After weighing, ignite again in a double porcelain crucible packed in charcoal within a clay crucible. The iridium recovered at this point is usually small, not more than 3 or 4 mg., equivalent to six or eight parts per thousand of the original sample. The loss in weight due to ignition in a reducing atmosphere is correspondingly small. For practical purposes, this ignition may be omitted and the first weight may be considered as iridium. The metal, however, is apt to contain a little platinum retained in the filter paper. It should be treated with dilute aqua regia to make sure that all platinum has been eliminated.

Evaporate the dilute aqua regia solution containing the platinum to dryness on a steam bath, add HCl to the residue and evaporate again to eliminate HNO_3, add a drop or two of hydrochloric acid and a few cubic centimeters of water, which should give a perfectly clear solution; if not, a little more HCl is required, but the amount must be kept as small as possible. Dilute the solution a little and pour it into 30 cc. of concentrated solution of pure ammonium chloride (10 g. NH_4Cl to 30 cc. H_2O). Stir well and let the solution stand at room temperature over night. Filter off the $(NH_4)_2PtCl_6$ and wash it several times with a cold 20 per cent solution of $(NH_4)Cl$. It is unnecessary to transfer the precipitate completely to the filter paper and the washing should be conducted with as little solution as possible.

It is not advisable to attempt to decompose the $(NH_4)_2PtCl_6$ by ignition. This always results in some loss in platinum carried away as a fine powder by the volatile decomposition products, however carefully the operation may be conducted. To avoid this source of error, it is better to precipitate the platinum as sulphide before ignition. Dissolve the $(NH_4)_2PtCl_6$ from the filter in very hot water, letting the solution run into the beaker in which the precipitation was made. Wash the filter thoroughly with water and dilute HCl, add 15 cc. of strong HCl to the filtrate, dilute it to 100 cc., heat it to boiling and pass a rapid current of H_2S into the hot liquid until all

platinum is precipitated as sulphide. Filter, wash with hot water, dry, ignite very carefully in a tared porcelain crucible, and weigh. The platinum should be wholly soluble in dilute aqua regia. If any residue remains, it is iridium which should be filtered off and weighed as described above, the weight being deducted from the platinum and added to the iridium obtained from the first dilute aqua regia solution. The iridium obtained from the dilute aqua regia solution calculated to the proper basis, should be added to the weight of iridium and osmiridium obtained from the original weighing, and the whole calculated to parts per thousand.

The ammonium chloride filtrate will contain most of the other metals of the platinum group, although it is probable that a small amount of these metals is also included with the platinum. The other members of the platinum group may be recovered as a whole by rendering the solution slightly alkaline, adding formic acid and boiling. A very small amount of platinum due to the solubility of $(NH_4)_2PtCl_6$ in concentrated or 20 per cent ammonium chloride solution is lost in the filtrate or included with the other platinum metals.

Selected Method for the Commercial Estimation of Platinum in Ores.—In the investigation of methods for the detection and estimation of platinum in vein material, the method following has been selected as satisfactory for commercial use. It contains nothing new, but has been compiled from various sources and is similar to one used by L. W. Dunham, Irvington, New Jersey.[1] The manipulation has been given in detail and notes added to explain the various steps in the process. Although a separation of the platinum metals is not given, the rough group separations are included to aid in determining the value of an ore.

Outline of Process.—The bead obtained by usual fire-assay methods may contain gold, silver, and the platinum metals and is parted with HNO_3. The silver and most of the platinum and palladium go into solution. The residue may contain gold, iridium, rhodium, and some ruthenium and osmium, as well as platinum. The gold and the rest of the platinum are dissolved from the residue of other platinum metals with dilute aqua regia and filtered off, leaving iridium, rhodium, part of the ruthenium, and a small amount of osmium, which may be ignited and weighed.

[1] From Davis, C. W., "The Detection and Estimation of Platinum in Ores," U. S. Bureau of Mines. *Tech. Paper* 270, 1921.

The HNO_3 solution may contain silver, platinum, and palladium. The silver is removed as the chloride, and the platinum and palladium are precipitated from the solution (which has been made slightly alkaline with Na_2CO_3), by boiling with formic acid, then filtered, ignited, and weighed. To separate the palladium from the platinum, the mixed metals are treated with warm dilute HNO_3, which dissolves the palladium and leaves the platinum. The palladium is found by difference, or may be precipitated with formic acid, after evaporating to dryness with HCl, taking up with water, and neutralizing with Na_2CO_3. The aqua regia solution is evaporated to dryness twice with HCl, taken up with water, and, after the gold is removed with oxalic acid, the platinum and palladium are recovered as above. A qualitative test is applied to a solution of the platinum precipitate.

Method of Procedure.—The ore in all cases is ground to pass a 100-mesh screen and when substances difficult to fuse, such as chromite and zircon, are present, the sample should be made to pass a 150-mesh screen.

When the quantity of platinum is small, it is advisable to run several samples of an assay ton each, combine the lead buttons, and scorify to about 30 g.

An assay ton of the carefully sampled ore is thoroughly mixed with a suitable flux. As iron has a greater affinity for iridium than has lead, the old iron-nail method of treating sulphide ores should not be used (see Table LII, giving typical assay charges which have been used in the estimation of platinum in different ores).

If there is not at least fifteen times as much silver as platinum in the ore, enough of a silver salt—chloride or nitrate—is added to make up the deficiency. The presence of excess silver is required to render the platinum soluble in HNO_3 when parting, to assist in removing the last traces of lead in cupelling and to lessen any tendency toward loss in the cupel. The addition of silver in the form of a salt makes possible a thorough mixing with the charge, and, when reduced, the numerous silver particles are distributed in a way to be most effective in collecting the platinum.

To an unknown ore about 0.05 g. of silver chloride may be added. The charge is fluxed as in the ordinary fire assay for gold and silver, except that after the fusion has become quiet the temperature should be raised somewhat higher than is the usual

practice and the heating continued for about an hour. The crucible is removed from the furnace without agitating the contents and left to cool. Cooling without agitation prevents loss of iridium, ruthenium, and osmiridium, which do not alloy with lead but sink through it and are held mechanically when the button cools. If the charge is poured, these metals are apt to be partly lost.

The button is freed from slag and cupelled at a high temperature. As the high temperature causes a loss of silver, a check or proof assay should be run at the same time to be used in correcting this error.

When platinum makes up over 1.6 per cent of the bead, the latter appears frosted to the unaided eye. The microscope will detect platinum when it constitutes 0.3 per cent of the silver bead. Considerable quantities of platinum make the bead flat and irregular. The roughness caused by iridium is of finer texture than that due to platinum. Palladium gives the surface of the bead an embossed appearance. Ruthenium in quantity turns the surface to a bluish-black color, a black scum being left on the cupel. After cupelling, the button is then parted with HNO_3, first with 1:4, then with 1:1, and finally with 2:1 acid. If gold, silver, and all the platinum metals are present in the ore, the silver, palladium, and platinum are dissolved by this treatment, leaving the gold, iridium, rhodium, and some ruthenium and osmium. Most of the osmium and part of the ruthenium are oxidized and lost during cupellation. Part of the iridium may not collect in the silver and will be lost on the cupel.

If considerable platinum is found, some will be left still undissolved. The residue is filtered off on a 5-cm., ashless filter paper, ignited, and saved for the recovery of any residual platinum as well as for the determination of iridium and rhodium.

Dilute HCl is then added to the filtrate slowly, with constant stirring to precipitate the silver. After this has set over night, the silver chloride is filtered off and washed with water, acidulated with HNO_3. If the precipitate is pink, it must be redissolved and again precipitated to remove occluded platinum or palladium. Although palladium may be separated from silver by one precipitation as the chloride, in acetic acid solution, the addition of the ammonia necessary to neutralize the HNO_3 present causes a bulk of salts on evaporation, which interfere with the subsequent operations.

Evaporate the filtrate just to dryness, do not bake; take up with dilute HCl and again evaporate just to dryness, then take up with dilute HCl, transfer to a 30-cc. beaker and evaporate nearly to dryness (until there is a dry spot in the center of the beaker). When cold, take up with a very little cold water and filter on a 5-cm. paper to remove the last traces of silver. It is important that all the silver be removed at this point, otherwise silver would come down on boiling with formic acid and vitiate the platinum-palladium result.

The filtrate is made slightly alkaline with Na_2CO_3, formic acid added, and the solution boiled in a covered beaker until all the platinum and palladium are precipitated (about 30 min.). These finely divided metals are filtered on a small (5-cm. or less) paper, washed with hot water, ignited, and weighed. As the platinum metals adhere to both glazed and unglazed porcelain crucibles on ignition, *impervite* crucibles may be used to advantage for the ignition of the finely divided metals. In transferring the platinum metals from the beaker to the filter, it has been found convenient to use a small wash bottle which will deliver a very fine stream of water. Funnels that have been cut down so that the small filter papers extend beyond the rim prevent the fine metals from creeping.

The filtrate should be boiled again with formic acid to confirm a complete precipitation of the platinum metals.

If the first parting solution is yellow or orange, the presence of palladium is indicated and the platinum may be separated from the palladium and determined. Warm the metals with dilute HNO_3 (1 to 4) which quickly and completely dissolves the palladium, filter, wash, ignite, and weigh the pure platinum. The palladium may be found by difference, or it may be precipitated by formic acid from the solution obtained by evaporating to dryness with HCl, dissolving in water, and neutralizing with Na_2CO_3.

The residue from HNO_3 parting (which may contain gold, iridium, and rhodium, as well as some ruthenium, osmium, and undissolved platinum) is treated with 1 to 5 aqua regia, dissolving the gold and platinum. The residual platinum metals are filtered off on a small filter paper, ignited (using *impervite* crucibles), and weighed. The aqua regia solution, which may contain gold and platinum, is evaporated to dryness, taken up with HCl and again evaporated to dryness, then extracted a second time

with HCl, evaporated nearly to dryness, taken up with cold water, and any residual matter is filtered off. The solution is then boiled with oxalic acid until the gold is all precipitated. It is well to let the solution stand overnight before filtering off the gold. The gold is filtered off and the platinum, recovered by boiling the solution, which has first been neutralized with sodium carbonate, with formic acid, is then filtered off, ignited, and its weight added to that of the platinum already found.

It is advisable to check results by running a known sample along with the unknown. This known sample is made by adding to a crucible charge the approximate quantity of gold, silver, and platinum found in the ore. The check is treated in every way the same as the sample to be examined, the latter being corrected if the known sample shows a discrepancy.

The resulting platinum and palladium should be dissolved separately in aqua regia, taken to dryness twice with HCl, extracted with water, and, after each solution has been acidified with HCl, tested qualitatively, KI giving a red color with platinum and a dark-brown precipitate with palladium.

Table LII.—Typical Assay Charges Used in the Estimation of Platinum in Different Ores

	Silicate	Hematite	Limestone	Roasted sulphide	Black sand largely Fe_3O_4[1]	Chromite, 40 per cent Cr_2O_3	Sulphides	Sulphides with barite
Ore, assay ton	1	1	1	1	1	1	1	1
Soda, grams	30–60	30	..	40	....	....	30–60	
Soda bicarbonate, grams	....	....	40	....	20	60	......	30
Borax, grams	....	....	20	20	....	....	10	20
Borax glass, grams	5	8	....	....	30	20		
Litharge, grams	60–90	70	40	40	66	35	50–150	150
Silica, grams	....	7	5	4	....	15	0–10	
Fluorspar, grams	....	....	....	....	....	....	....	15
Argols, grams[2]	2.5	3.5	2.5	7	4	3		
Niter, grams[2]	....	....	....	....	....	....	21	8
Silver chloride, grams	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Cover	Borax glass	Borax glass	Borax glass	Borax glass	Borax glass	Borax glass	Borax glass	Borax glass

[1] This charge has been used by A. A. Hanks and was kindly furnished by him. He prefers argols to any other reducing agent because in this flux the lead collects better by the use of this reagent.

[2] The quantities of niter or reducer are only approximate and must be so chosen that a 30-g. lead button is obtained.

In recent years several deposits have been discovered in South Africa, Canada, and in some of the Western United States, which carry palladium and platinum, the former often predominating, in amounts ranging from a trace to a few ounces per ton, associated with more or less gold, silver, and copper, but with negligible proportions of other platinoid metals. Hence, there is a demand for some rapid method of assay, using an assay ton or two, comparable in speed with the fire assay for gold and silver. The presence of a platinoid metal can usually be distinguished by the crystalline character of the bead obtained from a fire assay, a little silver having been added if necessary.

South African assayers find that, by parting with moderately strong and hot sulphuric acid, sufficient silver being present, and stopping the parting as soon as violent action ceases, practically all of the palladium remains with the gold and platinum. Preliminary amalgamation removes most of the gold. Further separations must depend on the same reactions as those given by Davis, variously applied, and involving precipitation of silver as chloride, gold by hot oxalic acid, platinum by strong solution of ammonium chloride, palladium by sodium iodide, or all of these by hydrogen sulphide or formic acid. Any of the precipitates can be filtered, burned, scorified, and cupelled with a little silver if necessary.[1]

[1] See also for detail on the rarer metals of the platinum group: Scott W. W., Standard Methods of Chemical Analysis. vol. I, 1925, article by R. E. Hickman.

CHAPTER XV

THE ASSAY OF ORES OF TIN, MERCURY, LEAD, COPPER, BISMUTH AND ANTIMONY

The assay of ores for base metal by fusion is still carried out in practice, especially for lead and tin. The fire assay gives, not the correct metal content, but the yield obtainable in smelting, although in metallurgic operations the yield may be greater or less. The smelter, therefore, purchases lead, tin, and copper ores on the basis of the dry or fire assay. The fire assay of copper is practically no longer in use, except in part of the Lake Superior district, on metallic copper concentrates, and in purchasing copper ores the assay is made by the standard electrolytic method, or a volumetric method, and a percentage of from 1 to 1.5 deducted to indicate dry assay. The usual deduction is 1.3 per cent. Thus the dry assay of copper on an ore is equivalent to the percentage obtained by the electrolytic method less 1.3 per cent.

While wet methods, with a deduction, will in all probability be employed eventually for all lead ores, as it is now for impure lead ores, pure lead ores are still assayed by the fire method. Tin ores almost invariably are assayed by the fire method, as the wet analysis of tin is long and tedious.

The Assay of Tin Ores.—The fire assay of tin ores is applicable only to those ores in which tin exists as cassiterite, the oxide (SnO_2). The chief reasons for inaccuracies in the fire assay of tin are:

1. Some of the tin, reduced in the assay from the oxide, is apt to be volatilized at the temperatures necessarily employed.
2. Metallic tin may be slagged by alkaline carbonates used in some of the methods of assay, forming stannates.
3. Foreign metals present in the ore are apt to be reduced and enter the button.
4. Sulphides present carry tin into the slag. If sulphates are present, they are reduced to sulphides.

5. Silica and silicates, always present in the ore, even after very careful concentration, carry tin into the slag, as silicate, while the SnO_2 passes through the lower stage of oxidation in being reduced to metallic tin.

6. The cassiterite, before reduction, is apt to combine with basic fluxes present in the assay, and be carried into the slag as stannates.

From this, therefore, it is evident that the fire assay for tin is only an approximation, although in many cases a very close one. If the result on a tin ore by the fire method checks that of the standard wet method (the modified Rose method[1]), it is to be ascribed to a balancing of errors, due to the presence of other metals in the ore, which have been reduced into the tin button.

Preparation of the Ore for Assay.—It is essential to remove all the gangue of the ore and have for the assay nothing but the cassiterite, as far as this is possible. The ore is roughly crushed on a buck board and put through a 40-mesh screen, crushings and screenings succeeding each other at frequent intervals in order to avoid the sliming of the cassiterite. If the ore is low-grade, *i.e.*, below 2 per cent Sn, 1,000 g. of the crushed ore is weighed out and carefully panned in a gold pan, the first pannings being saved for repanning. The ore is concentrated just as much as possible without incurring loss of cassiterite. The concentrates from the repanning of the tailings of the first treatment are added to the main lot of concentrates. Some or all of these will, unless the ore is very pure, contain probably garnets, feldspar, tourmaline, magnetite, zircons, wolframite, columbite, sulphides, quartz, etc. The concentrates are carefully transferred to a porcelain dish, dried, and roasted at a bright-red heat in order to decompose sulphides and sulphates. While the concentrates are still red-hot, they are transferred into a beaker containing water in order to make garnet and other silicates soluble (all except uvarovite), and after decanting water, treated with nitro-hydrochloric acid to remove most of the contaminating minerals, except quartz, wolframite, and some garnet. The concentrates are then filtered off and dried. If quartz is present, this can be removed by transferring the filtered concentrates to a platinum dish and treating with HF. This, however, will

[1] HOFMAN, "The Dry Assay of Tin Ores," *Trans.* A. I. M. E., vol. XVIII, p. 1.

rarely be necessary. The concentrates are then crushed in an agate mortar to pass a 100-mesh screen and treated as described below.

The Assay.—The two best methods for assay are the cyanide fusion and the German method, with black flux substitute. Of these two, the cyanide fusion is generally to be preferred, as any minerals still left in the cassiterite have less influence on the assay, and the loss of tin by volatilization is reduced to a minimum, on account of the low temperature employed.

The Cyanide Fusion.[1]—It is essential to use only the purest cyanide obtainable—the best sodium or potassium cyanide on the market for use in the cyanide process. Such impurities as K_2CO_3, sulphates, and sulphides in cyanide cause serious losses in the assay. The best alkaline cyanide to use is sodium cyanide, which may readily be procured at the present time. Some of the ordinary commercial cyanide known as "potassium cyanide" fuses at such a low temperature that the concentrates sink to the bottom of the crucible before reduction, and when reduction finally takes place the little globules of tin are found to be very difficult to collect. In order that the fusion may be successful, it is essential to follow directions closely. It is best to use 10 g. of concentrates, or an amount near that; usually the amount of concentrates obtained from the concentration of the ore approximates this if the proper amount of ore is chosen for concentration. Two grams of powdered cyanide are firmly tamped into a 20-g. crucible, the concentrates are mixed with 30 g. more of cyanide, placed in the crucible, and covered with 5 g. more. The crucibles are placed in the muffle at a full-red heat (750° C.), and are kept at this temperature for about 15 to 20 min. The charge will become very liquid, and will be a brown-red. The temperature should not be so high as to cause the cyanide to boil and evolve heavy fumes. It may, however, be kept too low, in which case the chemical reactions will not complete themselves and the tin will fail to collect into a button. If the concentrates still contain some foreign minerals, the fusion takes longer than 20 min. The crucibles are then withdrawn, cooled, and the button recovered by breaking the crucible. There will be two distinct slags, the lower one, surrounding the button, usually light green, amorphous and subtranslucent, and the upper one, or fused cyanide, opaque, milk-white and coarsely

[1] Hofman, *ibid.*

granular, soluble in water. The tin button should be white and soft; if not, it contains foreign metals.

The German Method.—The German method is based on the fusion of the cassiterite concentrates with charcoal and black flux substitute, which has the composition, two parts K_2CO_3, one part flour. Five grams of the concentrates are intimately mixed with 1 g. of pure wood charcoal and put into a No. D lead crucible or an ordinary 20-g. crucible. On top of this are placed 15 g. of black flux substitute, with which 1.25 g. borax glass have been mixed. Finally a pure salt cover is added, and a piece of charcoal, the crucible covered with a clay cover, placed in the muffle, and heated at a moderate heat until boiling of the charge has ceased, and then for ½ to ¾ hour more at a white heat. The crucible is then removed from the muffle, allowed to cool, and broken for the tin button. This should be white and soft, as in the cyanide fusion.

During the fusion, as the temperature rises, the charcoal reduces the stannic oxide to metallic tin, while any ferric oxide is reduced to ferrous oxide, if the heating is gradual, and is taken up by the slag. As the temperature rises, the flour in the black flux substitute partially decomposes, liberating carbon throughout the charge, which, as fusion takes place, prevents any stannic oxide not as yet reduced from uniting with the alkali of the flux. The slag, after cooling, should be crushed and planned for any prills of tin which have not entered the button. These are weighed and added to the weight of the button.

Results Obtainable.—Black Hills cassiterite concentrates, roasted, quenched, and treated with nitro-hydrochloric acid.[1]

Wet method of Rose-Chauvenet with K_2CO_3........	= 67.84 per cent Sn
German method..................................	= 67.58 per cent Sn
Cyanide method.................................	= 67.49 per cent Sn

Stream tin from Durango, Mexico,[2]

Wet method (Rose)..................	= 65.62 per cent Sn
German method....................	= 63.92 per cent Sn
Cyanide method.....................	= 65.19 per cent Sn

It is to be noted that while the dry methods approach very closely to the wet analysis, which gives the actual tin in the ore,

[1] Hofman, *ibid.*

[2] Miller, E. H., "The Assay of Tin Ores," "*School of Mines Quart.*," vol. XIII, p. 368.

the dry assay results are due more or less to a balancing of errors. Frequently dry assays will give higher results than the analysis; this is due usually to reduced iron.

Of the influence of foreign minerals left in the cassiterite concentrates, quartz has the worst, causing heavy losses. Feldspar and tourmaline have a similar effect, but not to so marked a degree. Mica and garnet give high results, due to the reduction of iron, although tin is lost in the slag. Columbite acts in a similar manner. With the German method the result is much

FIG. 59.—Apparatus required for the mercury assay.

more seriously affected by these impurities than with the cyanide fusion.[1]

The Assay of Mercury.—Mercury occurs in ores chiefly as cinnabar (HgS), and may with accuracy be determined by Chism's method.[2] For low-grade ores, the method is especially satisfactory, and has the advantage of being rapid and short. It is based on the fact that mercury is distilled from HgS, etc., in the presence of iron filings, and can be caught on silver-foil. The

[1] HOFMAN, *ibid.*

[2] CHISM, R. E., *Trans.* A. I. M. E., vol. XXVIII, p. 444.

Consult also, JAMES, G. A., *Eng. and Min. Jour.*, vol. XC, p. 800 and W. W. WHITTON, *Calif. Tech. Jour.*, Sept., 1904; *Mineral Ind.*, vol. XVII, p. 751.

difference in weight between the mercury-impregnated silver-foil and the foil before the assay gives the mercury. The apparatus required is as follows: (Fig. 59).

1. A small ring-stand.
2. A fire-clay annealing cup (No. B or C).
3. A piece of carefully annealed silver-foil 1.5 in. square, which is fitted and bent down to make a reasonably tight cover for the annealing cup. Gold foil is preferable to silver.
4. A flat silver or copper dish, holding 20 to 25 cc. of water. A round tin box with the tin sandpapered off the bottom answers very well.
5. A piece of asbestos board, 4 in. square and about 0.20 in. thick, in the center of which a circular hole has been carefully cut, into which the annealing cup will fit so as to project about 0.5 in. below the bottom of the board.
6. A small alcohol lamp, of about 60 cc. capacity.
7. A wash bottle with cold water, and a glass tube for a siphon. The silver foil is carefully fitted over the top of the annealing cup, the edges being bent down so as to make a close-fitting cover and prevent the escape of mercurial vapor. The silver dish should be polished on the bottom, and be in close contact with the foil, so that the cooling effect of the water will be fully transmitted.

The Assay.—For low-grade ores from 0.5 to 1 g. is taken and mixed with from 30 to 50 parts of iron filings. These filings should all pass a 40-mesh screen. A select lot of filings are best digested with alcohol for some time to remove oil and grease, then heated in a muffle to a dull-red heat for 10 min., cooled, and stored in a tight bottle. It is essential to have the filings free from oil and grease, else this will be deposited on the silver-foil with the mercury. The abrasive material known as "Diamond Crushed Steel" 40, 50, or 60 mesh is preferable to steel or iron filings. It is advisable to ignite it a minute or two in a closed crucible to expel organic matter. Powdered well-burned lime may be used, or a mixture of lime and iron. The amount of mercury in the ore should not be so great as to cause a too heavy coat on the silver-foil. For high-grade ores, not more than 0.1 to 0.2 g. should be used. Very small amounts of mercury can be detected by this method.

The ore, mixed with filings, is placed in the annealing cup, which is set into the asbestos board on the ring-stand, the silver-

foil weighed accurately, after igniting, to within 0.1 mg., and fitted to the cup, and the dish, filled with cold water, placed on the foil. The alcohol flame is then allowed to play just on the bottom of the cup, but not to spread around the sides. The flame should be about 1.25 in. high and is best shielded by a screen to steady it. The bottom of the crucible should not become more than a dull red, otherwise mercury will escape condensation. The time of heating should be from 10 to 15 min. It is best to heat for about 10 min., then cool, and reheat for 3 to 5 min. Longer heating than this causes loss of mercury. The degree and time of heat are very important.

During the heating the water in the dish should be replaced once or twice. It can easily be removed by a bent tube that has been filled with water, acting as a siphon. While the warm water is being removed, cold water is added from a wash-bottle. After the proper heating, the alcohol lamp is removed, the assay allowed to cool somewhat, the dish is removed, and at the same instant the silver-foil with the mercury is transferred by forceps to a desiccator and then weighed. The difference in the weight of the foil after and before the assay is the weight of the mercury, from which the percentage is calculated. The foil should then be ignited at a low red heat for 15 to 30 sec. and again cooled and weighed; it returns almost to its original weight but usually retains a trace of mercury. The foil can be used again after driving off the Hg at a red heat in the muffle, or with a Bunsen burner. A piece of foil can be used about six times. It should be weighed before each assay. The method also serves as a very sensitive and easily applied qualitative test on ores, if gold foil is used.

The following figures will serve to show the accuracy of the method.[1]

By Electrolysis from Cyanide Solution		By Chism's Method
Ore No. 1	12.37 per cent	12.44 per cent
Ore No. 2	67.26 per cent	67.23 per cent

The Assay of Lead Ores.—The fire assay of lead ores will probably pass out of use in time, just as the fire assay of copper has done.[2] At the present time it is still used, although for

[1] BACHELDER, G. N., in "*School of Mines Quart.*," vol. XXIII, p. 98.

[2] FULTON, C. H., Buying and Selling of Ores and Metallurgical Products, *Tech. Paper*, *83*. U. S. Bureau of Mines, 1915.

complex ores containing much copper or bismuth, or antimony with the lead, it is not in vogue. It is, however, still the criterion in the purchase of pure sulphide and oxidized lead ores, and also such complex ores as furnished by the Leadville, Colorado, district. Unoxidized ores of this type contain pyrite, blende, galena, some little chalcopyrite, and gangue. Oxidized ores contain cerussite, anglesite, calamine, limonite, etc., and gangue. The object of the assay is to bring the lead of these ores down into a button, free from other base metals, such as Cu, Zn, Bi, Sb, Fe, and free also from S and As. The loss of lead by volatilization and slagging and the reduction of base metals should be kept to a minimum. As already stated, this is a difficult thing to do; so that pure ores invariably will give low results, and impure ores frequently give high ones.

There are three methods of assay, differing in the flux used; (1) the lead-flux method; (2) the soda-argol method; (3) the cyanide fusion. Of these, the lead-flux method is chiefly used throughout the west. The soda-argol method is a good one on ores not basic. The cyanide method is only applicable to pure ores. With impure ores it tends to reduce other base metals, due to its powerful reducing action. Various mixtures of lead flux are used, of which three are made up as follows:

No. 1	No. 2	No. 3
4 parts $NaHCO_3$	2 parts $NaHCO_3$	6.5 parts $NaHCO_3$
4 parts K_2CO_3	2 parts K_2CO_3	5 parts K_2CO_3
2 parts flour	1 part flour	2.5 parts flour
1 part borax glass	1 part borax glass	2.5 parts borax glass

Flux No. 3 is probably the best for most purposes, as determined on a series of ores, the results with it being slightly higher.[1] For assay, 10 g. of ore (100-mesh fine) are mixed with 30 g. of flux, placed in a No. 6 or D crucible, or in a 20-g. crucible, covered with 8 g. more of flux, and put into the muffle at a low heat, which is then raised to a light yellow (1080° C.). The fusion should take about 30 to 35 min. Nails are added to the charge, two tenpenny nails for heavy sulphides, one for light sulphides or oxidized ores. When the charge is taken from the muffle, the nails are removed from the crucible by a pair of short hand tongs, care being taken to wash off all adhering lead globules. The crucible is then shaken and tapped thoroughly, and poured.

[1] McElvenny and Izett, in "The Chemical and Fire Methods of Determining Lead Ores," *Min. Rep.*, vol. XLVIII, p. 26.

The lead buttons are cleaned by hammering and then weighed. The percentage is obtained by multiplying by 10.

The reactions in the crucible are as follows:

$$7PbS + 4K_2CO_3 = 4Pb + 3(K_2S, PbS) + K_2SO_4 + 4CO_2$$
$$K_2S, PbS + Fe = Pb + K_2S + FeS$$
$$2PbO + C = 2Pb + CO_2$$

The carbon liberated in finely divided particles from the flour on heating reduces any lead oxides or carbonates in the ore, while the iron reduces lead from its sulphides and sulphates. The assay should check (in triplicate) within 0.5 per cent.

The soda-argol method uses the following flux:

$NaHCO_3$	6 parts
Argol	1 part

For 10 g. of ore, 35 g. of flux are taken, with a light flux cover. The fusion is performed as described for the lead flux method. The method is good on ores containing some silica, but not on basic ores or pure galenas, as all acid is lacking in the flux. A borax glass cover is best where the method is employed on basic ores.

In the cyanide method, pure cyanide should be used, and the temperature should be kept much lower than for the other two methods. For the regulation of temperature, reference is made to the assay of tin by the cyanide fusion.

For the fusion, 10 g. of ore are mixed with 35 g. cyanide, and a light cyanide cover used. Concerning the accuracy of the method the following figures are appended:[1]

Ore	Fire assay (lead flux), per cent	Gravimetric ($PbSO_4$), per cent
1. Galena	76	78.68
2. Galena	37	37.40
3. Cerussite	9	10.60
4. Pyrite, sphalerite, galena	24.7	18.46
5. Galena and stibnite	28.7	27.25
6. Cerussite	37.8	38.60

The Fire Assay of Ores Containing Native Copper.—The ancient Cornish method of assaying copper ores, which has been

[1] Bull, I. T., "Determination of Lead in Ores," *School of Mines Quart.*, vol. XXII, p. 348.

entirely abandoned, was a miniature smelting process closely following the smelting methods actually in use, and requiring experience and much personal attention. Full details of the procedure may be found in the works of Percy[1] and Mitchell.[2]

The Lake Superior fire assay is still in use in that region, and is a valuable process for ores containing coarse native copper. It is applicable to mine rock, mill concentrates, gravel and tailings, slags from reverberatories and remelting cupolas, or generally for material which cannot be accurately sampled or which contains copper in a form not easily gotten into solution for wet analysis. Sulphur compounds, in ore or flux, interfere with its accuracy.

Methods based on the specific gravity of mixtures are also used in determining the percentage of copper in ores and products containing much coarse native copper; large quantities, such as barrels or small carloads, being weighed under water and in air.

The fluxes tabulated are selected from a number given by Geo. L. Heath,[3] chemist to the Calumet and Hecla Consolidated Copper Company, as typical of those in use. All the fluxes should be pure and anhydrous, the soda was formerly prepared by heating and finally fusing sodium bicarbonate. The weight of material (65 g.) represents 1,000 gr., which was the standard weight, 500 or 2,000 gr. being used in some cases; the weights of fluxes have been here reduced to grams.

To save time the material is weighed wet. As soon as sampled it is dumped on a smooth wet board or vulcanite tray, about 15 by 20 in., mixed and flattened with a large spatula, and samples (usually nine dips) are taken with an 8-in. spatula and weighed on a pulp balance. The first is run for moisture and the second is thrown upon oiled or smooth paper. Here it is mixed with the flux, which may be weighed out or measured from a stock mixture, and transferred to crucibles, either Denver round form or Hessian or Battersea U triangular. Each charge is covered with a layer of cream of tartar 2 to 3 mm. ($\frac{1}{16}$ to $\frac{1}{8}$ in.) thick, and a tight cover is used on the crucible.

The pots are then placed in a furnace already heated, but not too hot, and are then rapidly heated by forced draft if coke is the fuel, or by natural draft with good soft coal. With soft coal the fire must be coaled and poked during the 15 to 20 min. required

[1] "Metallurgy of Copper," etc.

[2] "Practical Assaying."

[3] *Jour. Amer Chem. Soc.*, vol. XXIV, p. 699, August, 1902.

for quiet fusion. When quiet the pots are removed, allowed to cool quietly, and broken open. With practice the loss in slag can be kept very low (about 0.25 per cent) and almost exactly balanced by carrying a little iron into the copper button. A little metallic iron from the stamps is always found in mill products.

TABLE LIII.—CHARGES FOR ORES CONTAINING METALLIC COPPER

Material	Per cent copper	Per cent water	Grams sample	Grams of fluxes						Time in minutes
				Cream of tartar	Sodium carbonate	Borax glass	Old assay slag	Iron oxide	Silica	
Rich concentrate......	70 to 95	1 to 5	65	20	3 to 10	3	16	......	......	15 to 18
Leaner concentrate....	10 to 30	10 to 20	65	20	10 to 15	13	..	0 to 3	......	16 to 18
Slags or lean siliceous ore.........	10 to 25 5 to 10	0	65	25	20 to 25	20 to 25	..	0 to 13	0 to 10	16 to 20
Oxidized copper and iron ore (No S)	....	0 to 5	65	25	20	23	..	......	3 to 10	17 to 20

The Assay of Antimony and Bismuth Ores.—For accurate and satisfactory determinations on these ores, wet methods must be resorted to. Antimony occurs chiefly as the sulphide, stibnite, although the oxides and some native metal are found as ore. Bismuth as an ore occurs chiefly as the native metal, but is found also in combination with oxygen, sulphur, etc. For the assay, the following charge is best:

	Grams
Ore..	10
Cyanide....................................	40 to 50

Cover of cyanide

Fuse at a full red heat, as given for tin, for 30 min. The resultant buttons are brittle and cannot be hammered.

APPENDIX

TABLE LIV.—ATOMIC WEIGHTS

1928

	Symbol	At. number	At. weight		Symbol	At. number	At. weight
Aluminum	Al	13	*26.97*	*Mercury*	Hg	80	*200.61*
Antimony	Sb	51	*121.77*	*Molybdenum*	Mo	42	*96.0*
Argon	A	18	*39.94*	Neodymium	Nd	60	144.27
Arsenic	As	33	*74.96*	Neon	Ne	10	*20.183*
Barium	Ba	56	*137.37*	*Nickel*	Ni	28	*58.69*
Beryllium	Be	4	9.02	*Nitrogen*	N	7	*14.008*
Bismuth	Bi	83	*209.00*	*Osmium*	Os	76	*190.8*
Boron	B	5	*10.82*	*Oxygen*	O	8	*16.000*
Bromine	Br	35	*79.916*	*Palladium*	Pd	46	*106.7*
Cadmium	Cd	48	*112.41*	*Phosphorus*	P	15	*31.027*
Calcium	Ca	20	*40.07*	*Platinum*	Pt	78	*195.23*
Carbon	C	6	*12.000*	*Potassium*	K	19	*39.096*
Cerium	Ce	58	140.25	Praseodymium	Pr	59	140.92
Cesium	Cs	55	132.81	Radium	Ra	88	225.95
Chlorine	Cl	17	*35.457*	Radon	Rn	86	222
Chromium	Cr	24	*52.01*	*Rhodium*	Rh	45	*102.91*
Cobalt	Co	27	58.94	Rubidium	Rb	37	85.44
Columbium	Cb	41	93.1	*Ruthenium*	Ru	44	*101.7*
Copper	Cu	29	*63.57*	Samarium	Sm	62	150.43
Dysprosium	Dy	66	*162.46*	Scandium	Sc	21	45.10
Erbium	Er	68	167.7	*Selenium*	Se	34	*79.2*
Europium	Eu	63	152.0	*Silicon*	Si	14	*28.06*
Fluorine	F	9	*19.00*	*Silver*	Ag	47	*107.880*
Gadolinium	Gd	64	157.26	*Sodium*	Na	11	*22.997*
Gallium	Ga	31	69.72	Strontium	Sr	38	87.63
Germanium	Ge	32	72.60	*Sulfur*	S	16	*32.064*
Gold	Au	79	*197.2*	Tantalum	Ta	73	181.5
Hafnium	Hf	72	178.6	*Tellurium*	Te	52	*127.5*
Helium	He	2	*4.002*	Terbium	Tb	65	159.2
Holmium	Ho	67	163.5	Thallium	Tl	81	204.39
Hydrogen	H	1	*1.008*	Thorium	Th	90	232.15
Indium	In	49	114.8	Thulium	Tm	69	169.4
Iodine	I	53	*126.932*	*Tin*	Sn	50	*118.70*
Iridium	Ir	77	*193.1*	Titanium	Ti	22	47.90
Iron	Fe	26	*55.84*	*Tungsten*	W	74	*184.0*
Krypton	Kr	36	82.9	*Uranium*	U	92	*238.17*
Lanthanum	La	57	138.90	Vanadium	V	23	50.96
Lead	Pb	82	*207.22*	Xenon	Xe	54	130.2
Lithium	Li	3	6.940	Ytterbium	Yb	70	173.6
Lutecium	Lu	71	175.0	Yttrium	Y	39	*88.92*
Magnesium	Mg	12	*24.32*	*Zinc*	Zn	30	*65.38*
Manganese	Mn	25	*54.93*	Zirconium	Zr	40	91.22

TABLE LV.—CONVERSION TABLE FOR WEIGHTS

	Grains	Penny-weights	Troy ounces	Avoirdupois ounces	Avoirdupois pounds	Grams	Fine gold value	
							United States	British
One grain	1	0.041666	0.0020833	0.00228571	0.000142857	0.0648	4.306 cts.	2.125 pence
One pennyweight	24	1	0.0500	0.0548571	0.00342857	1.5552	$ 1.0335	4.25 shillings
One troy ounce	480	20	1	1.0971428	0.0685714	31.104	$ 20.67	85 shillings
One troy pound	5,760	240	12	13.165714	0.822857	373.248	$248.04	£51
One avoirdupois ounce	437.50	18.22917	0.911458	1	0.06250	28.35	$ 18.84	77.474 shillings
One avoirdupois pound	7,000	291.666	14.58333	16	1	453.60	$301.4375	£61.97
One milligram	0.015432	0.000643	0.00003215	0.000035274	0.0000022046	0.0010	0.06645 cts.	0.033 penny
One gram	15.432	0.643	0.03215	0.035274	0.0022046	1	66.45 cts.	2.73275 shillings
One kilogram	15,432	643	32.15	35.274	2.2046	1,000	$664.54	£136.64

TABLE LVI.—TABLE OF ASSAY VALUATIONS

Values	One part in	Per cent	Per metric ton			Per long ton of 2,240 pounds					Per short ton of 2,000 pounds	
			Troy ounces	U. S. dollars	Grams	Troy ounces	Ounces	Dollar-weight	Grains	U. S. dollars	Troy ounces	U. S. dollars
One per cent......	100	1	321.50	$6,645.40^{6}$	10,000	326.666	326	13	8	6,752.20	291.666	6,028.75
One gram per metric ton = one part per million..	1,000,000	0.0001	0.03215	0.66^{45}	1	0.03266	...	..	15.68	0.67^{5}	0.029166	0.60^{29}
One troy ounce per short ton.......	29,166.66	0.00342857 =24/7,000	1.1023	22.78^{45}	34.2857	1.120	1	2	9.6	23.15	1	20.67
One troy ounce per long ton........	32,666.66	0.0030612 =3/980	0.9842	20.34^{34}	30.612	1	1	..	.....	20.67	0.892857	18.45^{8}
One troy ounce per metric ton......	32,150	0.0031104 =2/643	1	20.67	31.104	1.016	1	..	7.7	21.00	0.90720	18.75^{2}
One dollar gold per short ton.......	602,875	0.00016587	0.0533285	1.1023	1.6587	0.054185	...	1	2	1.12	0.048379	1
One zolotnik per 100 poods.......	384,000	0.0002604	0.083724	1.73^{06}	2.604	0.08507	...	1	16.83	1.75^{8}	0.075954	1.57
One loth per centner............	3,200	0.03125	10.046875	207.66	312.5	10.2183	10	4	9	211.21	9.11458	188.14
One oitavo per quintal.........	16,384	0.00610	1.9623	40.56	61	1.9938	1	19	21	41.21^{18}	1.78654	36.80

TABLE LVII.—FINENESS OF BULLION AND ALLOYS OF PRECIOUS METALS

Denomination	Equivalent in millièmes or parts per thousand	
One carat	41.666	24 carats = 1 pound troy (England) 24 carats = 1 mark (Germany, etc.)
One grain per marc	0.217	4,608 grains = 1 marc of 8 ounces (France, Spain, etc.)
One ounce per marc	125.000	8 ounces = 1 marc (France, Spain, etc.)
One loth (silver)	62.500	16 loth = 1 mark (Germany, etc.)

TABLE LVIII.[1]—VOLUME AND WEIGHT OF FINE GOLD AND SILVER

	One cubic centimeter	One cubic inch	One cubic foot
Fine silver:			
Weight: grams	10.57	173.21	299,307.00
Weight: troy ounces	0.339825	5.5687	9,622.72
Fine gold:			
Weight: grams	19.3	316.269	546,513
Weight: troy ounces	0.6205	10.1680	17,570.39
Value: U. S. dollars	$12.8257	$210.17	$363,180
Value: pounds sterling	£2.647	£43.214	£74,674

[1] The foregoing tables originally published by SHARWOOD, W. J., *Mines and Minerals*, vol. XXIX, p. 250.

Bases of Computation.—The gram is taken as 15.4320 gr. The value of a troy ounce of fine gold is assumed as being exactly $20.67, instead of $20.6718346+, resulting in an error of less than 1 in 10,000. Values in English coin are based on the assumption that an ounce of fine gold is worth 4.25 pounds sterling, or 85 shillings, 1,020 pence; this is too high by about one part in 2,000, the true value being 1,019.45 pence. It is useless to attempt a closer approximation in ordinary work, for the simple reason that gold bullion assays are rarely reported closer

than the nearest half millième, or to within one part in 2,000. At the values adopted one dollar is equivalent to 4.11224 shillings, and one pound sterling to $4.86353.

Foreign and Obsolete Values.—The *adarme* (27.7 gr. or 1⁄16 of the Spanish ounce), sometimes used by Mexicans colloquially and especially with reference to placer work, is about 1.8 g., which in fine gold would be worth $1.20. For practical purposes, however, an adarme of ordinary gold may be taken as equivalent to $1, and this is exactly true for gold 830 fine.

Russian reports state values in *zolotniks* per 100 *poods*, but for low-grade placer deposits *doli* per 100 *poods* are used. As a *dola* is 1⁄96 *zolotnik*, we may take 1⁄100 of the values given in the table for the *zolotnik*, without serious error.

Marcos per cajon were formerly used in some South American countries, one *marco per cajon* apparently ranging between 100 and 70 parts per million. One *oitavo per quintal* corresponds practically to 2 oz. per ton.

The *loth per centner*, used in the older German works, corresponds to one part in 3,200, which is nearly 9 oz. per short ton or 10 oz. per long ton. In some cases there seems to have been a considerable variation from this ratio, the value sometimes being taken as one part in 3,520, or 10⁄11 of that used in these tables—the *centner* being then assumed as 110 instead of 100 pounds. The *quentchen* was 1⁄4, and the *denär* 1⁄16 of the *loth*.

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